

Arthur D Little

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**Advanced
Byproduct
Recovery:**

DEC 23 1995

O.S.T.

Direct Catalytic
Reduction of Sulfur
Dioxide to Elemental
Sulfur

Second Quarterly
Technical Progress Report
JAN - March 1996

DOE/PC/95252--T3

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Pittsburgh Energy Technology
Center
Under Contract #
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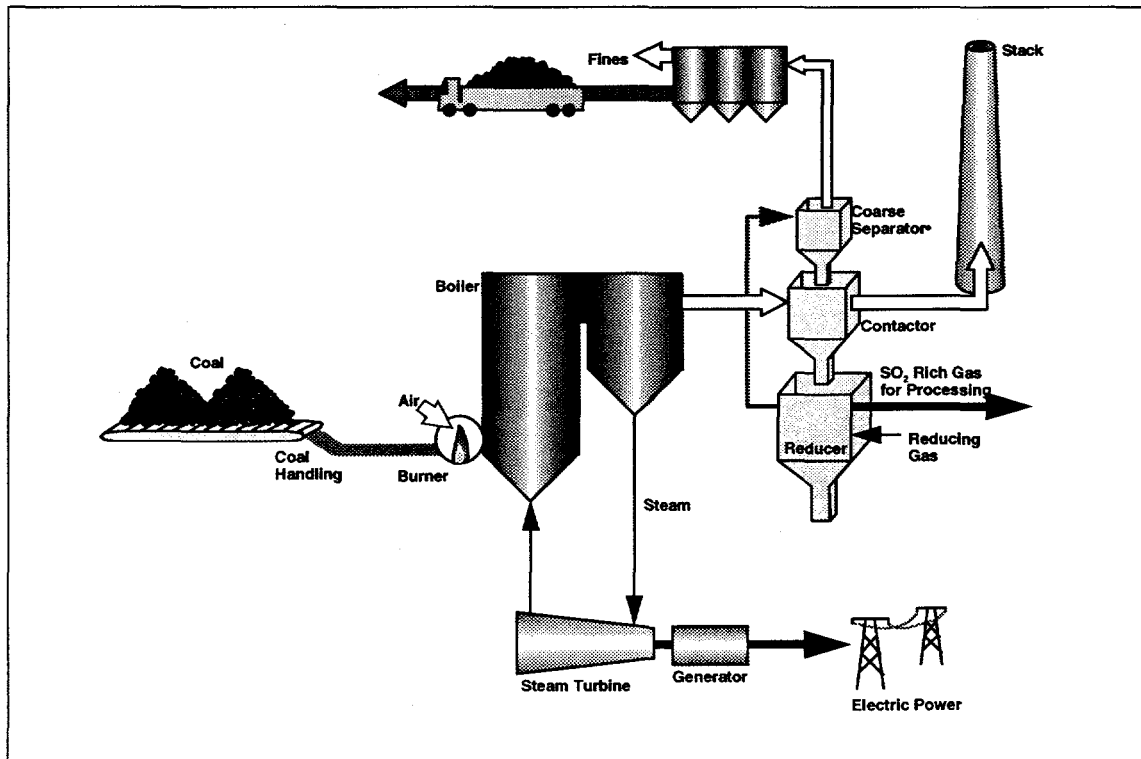
1. Introduction

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 construction¹. 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 gypsum² (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 annually³.

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 SO₂/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 SO₂ 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 CH₄ 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 SO₂ inlet concentration (0.1 to 10%) indicating its flexibility in treating SO₂ 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.

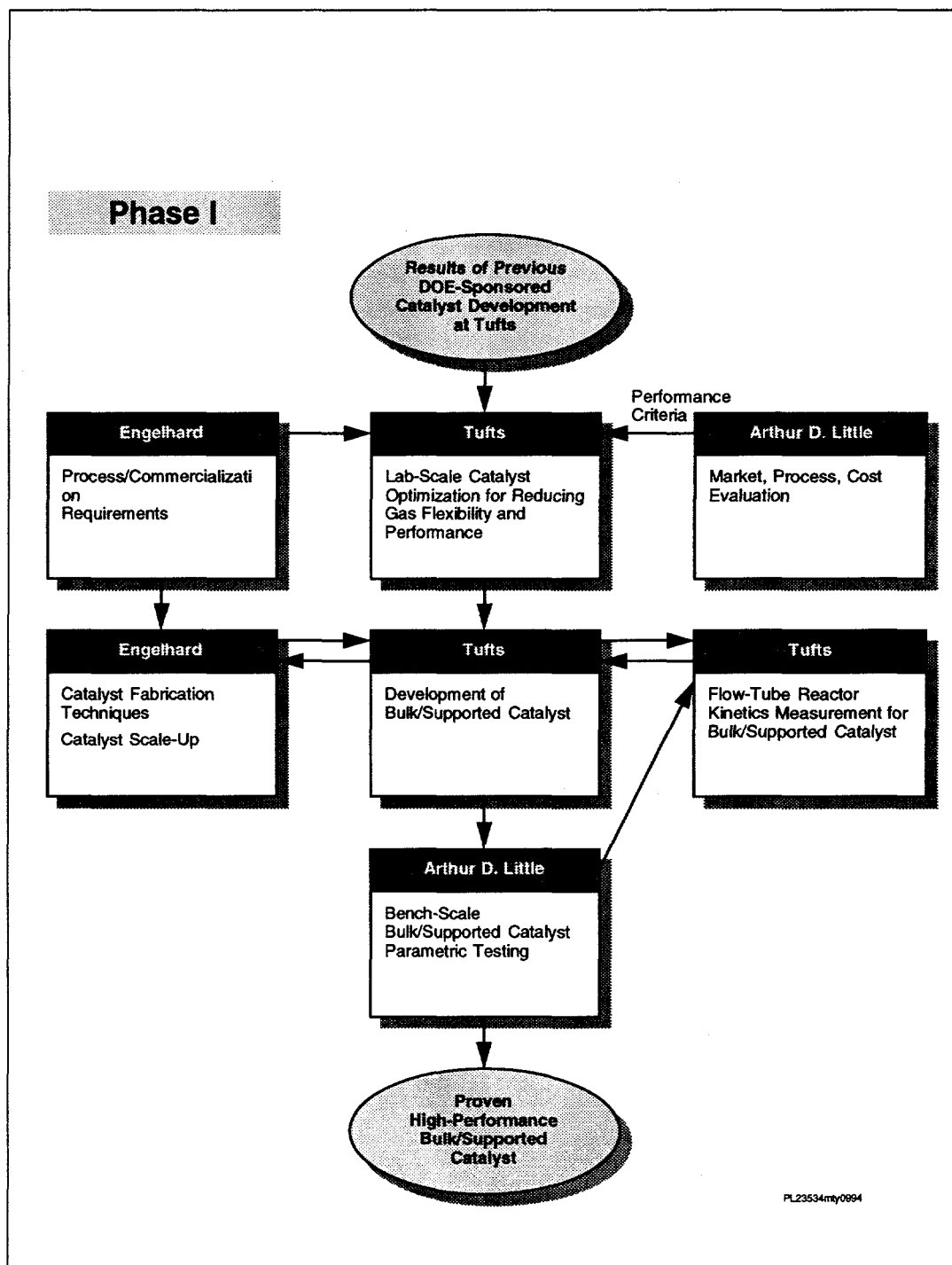
Lab-scale Catalyst Preparation/Optimization Studies. Catalyst will be prepared using a variety of methods (such as co-precipitation, sol-gel technique) from two candidate fluorite oxides (CeO_2 , ZrO_2) and four candidate transition metals (Cu, Co, Ni, Mo). These catalyst materials will be tested at Tufts in the same apparatus as was used in the previous work discussed above with a variety of reducing gases (CO , $\text{CO}+\text{H}_2$, 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 SO₂-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 SO₂ 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 SO₂ 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 SO₂ 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% SO₂ and 0.5% CH₄. 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% SO₂ and stoichiometric amount of synthesis gas with H₂/CO = 0.3, 2% H₂O and 2% CO₂; and
- (ii) wet feed gas mixture containing 1% SO₂, stoichiometric amount of synthesis gas with H₂/CO = 3, 2% H₂O, and 2% CO₂.

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 (H₂/CO ratios/CH₄) 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, SO₂ concentrations from 0.1% to 10%, H₂O contents from 0 to 10%, H₂/CO ratios from 0 to 3, and CH₄ 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 H₂O and CO₂ 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 SO₂ 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 (SO₂, H₂S 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: SO₂ concentration: 0.1 to 10%; H₂O concentration 2 to 30%; CO₂ concentration 2 to 30%; reducing gas composition: CO/H₂ ratio: 0.5 to 3.0; CO/CO₂ 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

Objectives:

- To manage the catalyst/process development effort;
- To coordinate the activities of three contractors;
- To prepare the required monthly, quarterly, topical, and final reports for DOE.

Approach:

This task will be conducted by ADL 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.

ADL shall establish and implement the reporting, meeting, and management systems to ensure a well-coordinated, documented, and successful program. Tufts and ADL will communicate through weekly teleconferences and monthly meetings. Tufts shall submit monthly progress reports to ADL and will prepare topical reports, as required, covering each completed research activity. Engelhard, ADL, and Tufts will communicate through quarterly visits for Engelhard staff to Cambridge, MA or Tufts/ADL staff to Engelhard's facility in New Jersey.

A Project Kickoff Meeting shall be held at PETC within the first 20 days following contract award. Formal project review meetings at PETC, including staff from ADL, Tufts, and Engelhard, will be held annually and at project milestones. ADL shall also attend the DOE Contractor Review Meetings to share results with other contractors working in related areas. ADL shall submit the reports listed in the DOE Reporting Requirements Checklist to PETC.

Deliverables:

Reports and presentation materials from formal project meetings.

3. Objectives for Second Quarter Activity

The objectives for the second quarter were to:

- Initiate the market, process and cost evaluation work. To identify the regenerable sorbent technologies that could benefit from advanced byproduct recovery. To establish the key technical and economic criteria that must be met by the catalytic SO₂ reduction process.
- Begin screening microreactor tests, using CH₄/SO₂/He gas mixtures. Conduct parallel studies of the reducibility of these oxide composite by temperature-programmed reduction. Perform elemental analysis of the catalysts by Inductively Coupled Plasma emission spectroscopy (ICP). Analyze the catalysts produced to date by X-ray diffraction analysis.

The focus of this report is on the initial results of the market, process and cost evaluation. Detailed initial results of the catalyst screening tests at Tufts will be presented in the next quarterly report.

4. Second Quarter Technical Progress

4.1 Process, Market and Cost Evaluation

4.1.1 Task 1 Elements/Objectives

The scope of this task can be broken down into three major elements as follows:

- ***Define technical requirements.***
 - ◇ concentration and variability of offgas stream main constituents
 - ◇ offgas stream contaminants
 - ◇ preferred reducing gas
 - ◇ emissions limitations
 - ◇ reliability/durability issues
- ***Identify and outline critical market forces.***
 - ◇ current FGD technologies and costs
 - ◇ trends in FGD technology development, applications and costs
 - ◇ extent to which an advanced, one-step, sulfur byproduct conversion process improves competitiveness of SO₂ recovery technologies
- ***Prepare a process cost evaluation.***
 - ◇ develop preliminary capital and operating costs
 - ◇ compare costs with alternative, available technologies

4.1.2 Subtask 1 - Define Technical Requirements

Efforts during the first quarter of 1996 focused on:

- concentration and variability of offgas stream main constituents;
- offgas stream contaminants; and,
- preferred reducing gas.

A survey was conducted to develop a compendium of: 1) flue gas desulfurization (FGD) technologies capable of producing enriched streams of recovered SO₂; and, 2) processes capable of converting the recovered SO₂ to elemental sulfur. The survey focused on identifying those processes that have achieved commercial application; have attained an advanced stage of development (typically successful prototype testing), whether still actively being pursued or not; or, are currently under active development at a level beyond laboratory scale. The purpose of the survey was twofold. First, to establish the database for the range of potential feedstream conditions and most probable, or preferred, reducing gases. And, second, to begin to develop the background information for assessing the market potential for one-step SO₂-to-sulfur conversion technology.

The survey drew upon four principal sources of information:

- available DOE reports;
- ADL in-house files;
- publications over the last fifteen years identified through a literature search; and
- selected contacts of individuals within DOE, system suppliers, and industry organizations as well as experts who have been involved in the field of FGD over the past ten to twenty years.

Preliminary Survey Results

Tables 4-1 through 4-3 summarize the initial results of this survey. This summary is considered preliminary at this time. It will continue to be updated with additional information obtained over the next three to six months.

At the risk of oversimplification, advanced FGD technologies producing an enriched SO₂ byproduct stream generally fall into four major groups, although most of these have subgroups that further differentiate general process approaches.

- ***Aqueous alkaline scrubbing.*** There are two subgroups: alkaline metal-based and ammonia-based.
 - ◊ Alkaline metal-based - Many of these processes were developed in the 1970s and 1980s. The two that achieved the highest degree of commercialization in were the Wellman Lord process and the numerous variations of the MgO process; although only the Wellman-Lord process was ever used to produce elemental sulfur in an application on combustion flue gases. Neither is currently being marketed. The only process currently being actively pursued is the ELSORB process, an offshoot of the Wellman Lord technology, but it has not been demonstrated in the U.S.
 - ◊ Ammonia-based - Most all of the development work on ammonia-based technology over the past ten to fifteen years has been outside the U.S.; and some of this work has focused on generating an SO₂ byproduct stream for conversion to acid or sulfur. Interest has recently been revived in Europe and the U.S. in ammonia scrubbing, but primarily focused on producing ammonium sulfate for fertilizer.
- ***Organic absorption.*** This group also has two major subgroups: amine-based processes and citrate-based processes.

Table 4-1 FGD Technology and Status Summary

Technology	Developer and/or Current Supplier	Sorption			SO ₂ Conversion	Application Focus		Current Status	Development Status	
		Sorbent	SO ₂	H ₂ S	NO _x	Regeneration	Steam Boilers	IGCC	Process	Extent of Development
Aqueous Metal/Alkali										
MagOx	PECO/Raytheon; Kawasaki Mitsui/GEESI Davy Environmental	Mg(OH) ₂ /MgSO ₄ Na ₂ SO ₃	●	---	---	Direct-Fired Thermal	●	---	---	C: Utility (Acid)-US;Europe;Japan
Wellman-Lord			●	---	---	Thermal (Indirect Steam)	○	---	●	C: Utility (Acid)-US;Europe
ELSORB	Elkem	Sodium Phosphates	●	---	---	Thermal (Indirect Steam)	○	---	●	C: Refinery (Claus)-Global
ACP	Rockwell/ABB	Na ₂ CO ₃	●	---	---	Molten Bath Reduction	●	---	---	C: Refinery (Claus)-Europe
SOXAL	Allied-Signal (Aquatech)	Na ₂ SO ₃	●	---	---	Electrodialysis	●	---	---	P: Utility-Europe
SULF-X	PENSYS/DOE	Iron Sulfides	●	---	●	Thermal (Indirect Coal)	●	---	---	D: Utility-Abandoned
Aqueous Ammonia										
Cominco	Cominco/Olin-Mathieson	Ammonia	●	---	---	Acidification/Stripping	○	---	●	P: Utility-US
ABS	TVA	Ammonia	●	---	---	Acidulation/Stripping/Thermal	●	---	---	D: Utility-Abandoned
Catalytic/IFP/CEC	Catalytic/IFP/CEC	Ammonia	●	---	○	Acidulation/Stripping/Thermal	●	---	---	D: Utility-Abandoned
Amine-Based Scrubbing										
DMA	ASARCO	Dimethylaniline	●	---	---	Thermal (Indirect Steam)	---	---	●	C: Smelter; Chemical (Acid)-US
CANSOLV	Union Carbide	Triethanolamine	●	---	---	Thermal (Indirect Steam)	●	---	●	P: Refinery-Abandoned
Dow Process	Dow Chemical	Proprietary Amine	●	---	○	Thermal (Indirect Steam)	●	---	●	D: Utility (Catalytic/IFP)-Europe
Solinox		Polyethylene Glycol	●	---	---	Thermal (Indirect Steam)	●	---	●	P: (CEC NO _x portion)-Japan
NOSOX	Monsanto	Ethanolamine Glut.	●	---	---	Thermal (Indirect Steam)	○	---	●	C: Smelters (Acid/Liquid SO ₂)
Citrate-Based Scrubbing										
Stauffer	Bureau of Mines/Stauffer	Sodium Citrate	●	---	---	Liquid Phase	○	---	●	P: Absorption/Regeneration only
Pfizer	Bureau of Mines/Pfizer	Potassium Citrate	●	---	---	Liquid Phase	○	---	●	P: Absorption/Regeneration only
Zinc-Based Adsorbents										
HGD	General Electric	Zinc Ferrite	●	●	---	Dilute oxygen	---	●	---	P
DSRP	DOE(METC)/RTI	Zinc Titanate	●	●	---	Dilute oxygen	---	●	---	L
ELSE	Amoco		●	●	---	Dilute oxygen	---	●	---	P
Z-Sorb	Phillips	ZnO (Ni-Promoted)	●	●	---	Dilute oxygen	---	●	---	P
Other Metal Adsorbents										
Copper Oxide	DOE(PETC)/TECO	CuO/Alumina	●	---	●	H ₂ or Methane	●	---	---	D: Utility-US
Alkali-Based Adsorbents										
Sorbtech	Sorbtech	MgO/Vermiculite	●	---	●	Thermal (Reducing Atm.)	●	---	---	D: Utility-US
NOXSO	NOXSO	Na ₂ CO ₃ /Alumina	●	---	●	Thermal (Oxidizing Atm.) H ₂ CO(Methane)-Steam	●	---	---	D: Utility-US
Physical Adsorption										
Bergbau-Forschung	Mitsui/Uhde/GEESI	Activated Char	●	---	○	Carbon	●	---	---	C: Utility (Acid)-Germany;Japan
EPDC	EPDC/Sumitomo	Activated Char	●	---	●	Carbon	●	---	---	D

Key: ● Principal Focus ○ Secondary/Adjunctive Focus
 Active - Currently pursuing commercial contracts and/or continuing development
 Passive - Responding to opportunities but not pursuing contracts
 Inactive - Not currently participating actively in the market or development of technology
 Abandoned - Technology no longer pursued or offered

Table 4-2 FGD Technology and Status Summary (continued)

Technology	Developer (Current Supplier)	Regeneration	Pretreatment	Product Gas Conditions					
				T(°C)	Composition (mol %)				Other Constituents
					SO ₂	H ₂ S	CO ₂	H ₂ O	N ₂
Aqueous Metal/Alkali MagOx Wellman-Lord ELSORB ACP SOXAL SULF-X	PECO/Raytheon; Kawasaki	Direct Thermal (Fluid Bed or Klin) - Oxidizing	Solids Removal	360±20	15±2	---	15±2	20±4	Balance
	Mitsui/GEESI	Direct Thermal (Fluid Bed or Klin) - Reducing	Solids Removal	360±20	16±2	---	14±2	20±4	Balance
	Davy Environmental	Thermal (Indirect Steam)	Condensed	25±5	92±6	---	Trace	Balance	Trace
	Elkem	Thermal (Indirect Steam)	Condensed	25±5	92±6	---	Trace	Balance	Trace
	Rockwell/ABB	Molten Bath Reduction with Coke	NA	NA	---	---	---	---	---
Aqueous Ammonia Cominco ABS Catalytic/IFP/CEC	Allied-Signal (Aquatech)	Electrodialysis	None	NA	---	---	---	---	---
	PENSYS/DOE	Indirect Thermal (Coal)	None	NA	---	---	---	---	---
	Cominco/Olin-Mathieson	Acidification (H ₂ SO ₄)/Steam Stripping	Condensed	25±5	92±6	---	Trace	Balance	Trace
	TVA	Acidulation/Steam Stripping							
	Catalytic/IFP/CEC	Acidulation/Steam Stripping + Liquid Claus (IFP)							
Organic-Based Scrubbing DMA CANSOLV Dow Process Solinox NOSOX	ASARCO	Thermal Stripping (Indirect Steam)	Condensed	25±5	92±6	---	Trace	Balance	Trace
	Union Carbide								
	Dow Chemical								
	Monsanto								
	Bureau of Mines/Stauffer	H ₂ with Liquid Claus	NA	NA	---	---	---	---	---
Citrates-Based Scrubbing Stauffer Pfizer	Bureau of Mines/Pfizer	Dilute oxygen	None	750±20	1-2	---	Trace	---	Balance
Zinc-Based Adsorbents HGD DSRP ELSE Z-Sorb	General Electric								
	DOE(METC)/RTI								
	Amoco								
	Phillips								
	DOE(PETC)/TECO	H ₂ Methane	Condensed Condensed	25±5 25±5	92±6 60-65	Trace Trace	---	Balance 2-10	---
Other Metal Adsorbents Copper Oxide									
Alkali-Based Adsorbents Sorbtech NOXSO	Sorbtech	Thermal (Reducing Atm.)	None	750	65±?	30±?	---	Trace	---
		Thermal (Oxidizing Atm.-Air)	None	550	65±	25±	---	Trace	Balance
			None	640	65±	30±	---	Trace	---
			None	640	65±	30±	---	Trace	---
	NOXSO	Methane	None	640	65±	30±	---	Trace	---
Physical Adsorption Bergbau-Forschung EPDC	Mitsui/Uhde/GEESI	Coke/Coal	Condensed	25±5	50-60	---	30-35	Balance	Trace
	EPDC/Sumitomo	Coke	None	400	15±	Trace	5±	20±	Balance

Table 4-3 Sulfur Production Technologies Status Summary

Technology	Developer and/or Current Supplier	Conversion/ Reductant	Linkage to Sorption Technology	Development Status		Feed Gas Requirements	
				Extent of Development	Current Status	T(C)	Composition
Gas Phase Direct Coke/Coal RESOX EPDC Outokumpu	Foster Wheeler/Uhde/Mitsui? EPDC/Sumitomo Outokumpu	Coke or Coal Coke Coal	Bergbau-Forschung (Decoupled)	D C: Smelter-Abandoned?	Active Active Abandoned		
Reducing Gas Allied Chemical Texas Gulf Sulfur Outokumpu DSRP Parsons FGC	Allied Chemical Texas Gulf Sulfur Outokumpu DOE(METC)/RTI Parsons Process Group	Methane or synthesis gas Methane Methane or synthesis gas ? H ₂ , fed directly into flue gas for catalytic conversion of SO ₂ to H ₂ S Indirect thermal regen. in reducing atm. (750 C) or in oxidizing atm. (550 C), then to mod. Claus -- proprietary Sorbtech tech. under devel. Multi-stage regen. using H ₂ or methane to produce H ₂ S and SO ₂ for Claus feed	None None None DSRP (Decoupled) Parsons FGC (Coupled)	C: Utility(US)-Abandoned P P P P	Passive Passive Abandoned Active Inactive Active		
Sorbtech	Sorbtech		Sorbtech Proprietary or Claus	P	Active		
NOXSO	NOXSO		NOXSO and Claus	D: Utility(US)	Active		
Other IFP SULF-X	Catalytic/IFP/CEC PENSYS/DOE	H ₂ with Liquid Claus Indirect calcination of FeS at 700±50 C with some coke	Catalytic/IFP/CEC (Decoupled) SULF-X (Coupled)	D: Utility(Europe) P	Passive Inactive	NA NA	
ACP	Rockwell/ABB	Molten bath reduction of salts with coke	ACP (Coupled)	D: Utility(US)-Abandoned	Inactive	NA	
Citrate Processes	Bureau of Mines/Stauffer/Pfizer	H ₂ with Liquid Claus	Citrate (coupled)	C: Smelter(US)-Abandoned	Inactive		

* Technologies that are potential direct competitors in conversion of enriched SO₂ streams as well as technologies that could compete indirectly by supplanting the need for decoupled gas phase SO₂ conversion

- ◇ Amine-based - Numerous amine-based technologies have been developed over the years, dating to the 1950s. Most were developed for applications in ore smelting and the petroleum industry. Some attempts were made to advance and commercialize the technology for application to utility FGD, with little success due to the relatively high costs of fully integrated systems to produce either acid or sulfur. (Refineries already had embedded Claus sulfur conversion processes and smelters produced acid.) Few, if any, commercial applications remain and no processes are being actively marketed for combustion FGD.
- ◇ Citrate-based - This technology development was actively supported by the U.S. Bureau of Mines, again with a focus on smelting applications. For the most part, continued commercialization of this technology has been abandoned.
- **Reactive adsorption.** This group is comprised of three principal subgroups. Although no processes have achieved commercialization, efforts in all of these subgroups actively continues.
 - ◇ Zinc-based adsorption - There are four technologies currently being pursued, primarily for application to IGCC. Much of this work is being funded by the U.S. DOE.
 - ◇ Copper oxide - This process dates to the 1970s and has undergone significant evolution and advancement over the past 25 years. The U.S. DOE continues to be a principal supporter of the technology development with a pilot unit at PETC and plans for a demonstration unit.
 - ◇ Alkali metal-based - Two processes based upon the use of alkali metal adsorption are in advanced stages of development, Sorbtech and NOXSO. Both are combined SO_2 and NO_x approaches specifically focused on application to the utility FGD market; and, both have integrated or closely coupled technology for sulfur conversion. Demonstration units for these processes are underway.
 - ◇ Physical (carbon-based) adsorption - These technologies also have a long development history. Most of the recent efforts (over the past ten to fifteen years) has been outside the U.S. The focus has been on conversion of the byproduct SO_2 to elemental sulfur using coke or high-grade coal as the reducing agent. No demonstration units are currently planned in the U.S.

Evaluation of Technical Requirements

With the possible exception of the alkali metal-based reactive adsorption processes, notably Sorbtech and NOXSO, most all of the technologies could benefit from an efficient, cost-effective, one-step sulfur conversion technology. As shown in Table _____ the range of conditions of the byproduct SO₂ streams vary widely -- from highly concentrated streams (95%+) at low temperature with residual moisture, to fairly low concentration streams (<20%), some at high temperature with various levels of "contaminants".

In order to focus research and development efforts, we are in the process of prioritizing the FGD technology groupings to establish a profile of feedstream characteristics most representative of commercialization needs. Consideration is being given to a variety of factors including: the FGD technology development status; the benefits/importance of an add-on sulfur conversion technology to the commercialization of the technology; the current level of support in advancing the technology; and, in concert with the assessment of the critical market forces, the perceived opportunities for the FGD technology were it to be successfully demonstrated.

The initial "cut" at this prioritization places technologies into two general categories.

Primary: Technologies in this category are ones at advanced stages of development and which continue to be actively pursued, or technologies which have been commercialized and continue to be actively marketed; but, only those without close-coupled sulfur conversion processes.

- Zinc-based technologies - Currently pursued as the technology of choice for IGCC applications.
- Copper oxide process - One of the most advanced technologies for byproduct SO₂ that continues active development.
- Carbon-based adsorption - Well-advanced technology that has been through demonstration programs.

Secondary: These are technologies that have achieved a significant level of commercialization (defined as a number of installations which are still operated) but are not now actively marketed; or have progressed through pilot testing and offer significant potential advantages, but whose development is currently stalled.

- Selected aqueous alkali processes - As a group these have not fared especially well for sulfur conversion and currently only the ELSORB and SOXAL processes are being actively pursued.
- Ammonia scrubbing - Most of the applications for ammonia scrubbing are for fertilizer byproducts; however, the potential remains for conversion to sulfur.
- Selected amine-based processes - Two of these may offer significant advantages to prior processes, the Dow technology and CANSOLV.

We are now developing more detailed information regarding the range of conditions of the byproduct SO₂ 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.

4.1.3 Subtask 2 - Identify and Outline Critical Market Forces

In concert with the development of the technical requirements, work began on identifying and outlining the critical market forces relative to commercial acceptance of a one-step sulfur conversion technology. This effort is being undertaken on a global scale, rather than being limited to the U.S. because of the importance of emerging international markets and the continuing interest outside the U.S. in the development of sulfur-producing FGD technology. While the focus is on utility applications, consideration is also be given to other potential markets on an opportunistic basis as these are identified.

Obviously, there are a wide variety of FGD technologies being installed around the world on utility power plants and industrial boilers. And, there continues to be interest in recovery technologies that produce acid or elemental sulfur; however, few, if any, are actually being selected for commercial installations. The intent of this analysis, which will continue through the next two quarters, will be to determine what the principal competing FGD technologies will be over the near term (next five years) and the intermediate term (five to fifteen years), and forecast where and how sulfur producing technology will fit in. An important aspect will be whether a one-step conversion process will play an important role in the competitiveness of producing sulfur from FGD.

Preliminary Assessment of Short-Term Market

The following represents our preliminary assessment of the near-term (5-7 years) market for FGD technologies in the electric utility industry, the refining and chemical industry, and the ore smelting industry. It should be emphasized that the one-step sulfur recovery technology under development will not be available commercially in this time-frame.

- There are currently no commercial sulfur-producing FGD technologies in use anywhere in the world (the system at Public Service of New Mexico was converted to acid production approximately 10 years ago).
- Only three power plants in U.S. produce enriched byproduct SO₂ for conversion to acid.
- 1990 Clean Air Act Amendments (CAAA) Phase I FGD installations heavily favored gypsum-producing FGD: 70% of capacity went to commercial grade (capable) gypsum production and the rest went to technologies producing stabilized sulfite waste for disposal.
- We predict FGD installations over the next four to five years to be no more than 10,000 - 15,000 MW maximum. Most of this capacity will derive from CAAA Phase II requirements (8,000 - 10,000 MW) and the lion's share will be limestone, forced oxidation to produce commercial grade gypsum. The utility industry is currently highly capital averse, being driven by ongoing deregulation initiatives and stiff competition from independent power producers.
- The predominant FGD technologies deployed over the next five years or so are expected to be limestone, forced oxidation to produce commercial grade gypsum for the larger retrofits and new units; lime spray drying and lime circulating beds for medium/small units; and ammonia-based fertilizer systems for conversions (e.g., Orimulsion) and some retrofits. As the gypsum market becomes saturated, other recovery technologies will become favored.
- Oil refineries are not promising short-term (5-7 years) markets for new sulfur recovery technologies. Most refineries have Claus or other sulfur conversion technology already in place and no major expansions in refinery capacity or requirements in the U.S. are envisioned in the short term.
- Ore smelting applications are also unlikely to offer much opportunity in the short term as most smelters already have systems for producing acid. Steel, aluminum, copper and zinc comprise 98% of the U.S. smelting market:
 - ◊ large integrated *steel mills* are being shut down or production is being curtailed in favor of mini-mills that reprocess scrap steel.
 - ◊ *aluminum smelting* does not involve SO₂ control.
 - ◊ *copper smelting* is moving toward hydrometallurgical technology to process "tailings".
 - ◊ *zinc smelting* is now focused on battery recovery which is not conducive to SO₂ byproduct conversion to sulfur.

- Many industrial boilers are generally not large enough to give favorable economics for current sulfur recovery technologies.

The above assessment is provided for background information. The SO₂ reduction technology under development is aimed at the next generation of highly-efficient regenerable FGD technologies which have yet to reach the market.

4.2 Catalyst Preparation and Characterization

The oxidation-reduction properties of transition metal modified fluorite-type oxides (CeO₂ and stabilized ZrO₂) were studied by temperature programmed reduction (TPR) by H₂ and CH₄, as well as temperature programmed desorption of oxygen. Transition metals chosen for initial studies were Cu, Co, and Ni. Dopants used to increase oxygen vacancy concentration and stabilize the fluorite structure were La for CeO₂ and Y for ZrO₂ based catalysts. Dopant concentration was fixed at 4.5% in all catalysts tested. TPR studies indicate the presence of two main reduction peaks in CeO₂ based catalysts, one being reduction of transition metal oxide and the second being the reduction of CeO₂. CeO₂ reduction temperature was lowered by the addition of dopant and transition metal, e.g. from 650°C to 600°C. On both CeO₂ and ZrO₂ based catalysts the Cu reduction peak was at about 100°C when H₂ was used as a reducing gas and at about 400°C when CH₄ was used as a reducing gas.

In addition, during this period analytical techniques for gas chromatography were established. A Chromosil 310 gas chromatograph column at 50°C was used, with helium carrier gas at a flow rate of 30 cm³/min for the TCD detector and nitrogen carrier gas at a flow rate of 30 cm³/min for the FPD detector. During this period all necessary calibrations of the TCD and FPD detectors were performed.

15%Cu-Ce(La)-O, 15%Co-Ce(La)-O, 15%Ni-Ce(La)-O, and Ce(La)O₂ were chosen for initial activity tests. All activity tests were carried out in the laboratory-scale, packed bed flow reactor, which consists of a 0.5 in diameter x 18.5 in long quartz tube with a porous quartz frit placed at the middle for supporting the catalyst. Initial activity tests were performed under the following conditions: stoichiometric amount of reacting gases, which consist of 1% SO₂ and 0.5% CH₄ (balance He) at a total flow rate of 100 cm³/min. The contact time was 0.09 gs/cm³. Typically, catalysts were reduced for one hour 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-down behavior were examined to check for possible hysteresis.

Ni, Co, Cu, Mn, Cr, and Fe containing Ce(La)O₂ and Zr(Y)O₂ catalysts, as well as pure CeO₂ and Ce(La)O₂ were tested using reacting gases at stoichiometric ratio (1% SO₂ and

0.5% CH₄ balance He). All tests were performed at a gas flow rate of 100 cm³/min at contact times of 0.09gs/cm³ and 0.18 gs/cm³ in the temperature range 500°C to 750°C. Ni-Ce(La)-O catalyst showed the highest activity.

Further studies will include more detailed investigations of Ni-Ce(La)-O catalysts with respect to the effects of space velocity and SO₂/CH₄ ratio.

5. Plans for Next Quarter

5.1 Catalyst Development Work

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.

5.2 Process Evaluation Work

We will develop more detailed information regarding the range of conditions of the byproduct SO₂ 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.

We will examine the potential of the one-step SO₂ reduction process for enhancing the commercial prospects of recovery FGD technologies.

We will begin to prepare process cost evaluations for the proposed one-step SO₂ reduction process.

5.3 Bench-Scale Testing

We will 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.

6. References

1. Steam Electric Plant Factors, 1992 Edition, National Coal Association.
2. "Commercial Utilization of SO₂ Removal Wastes in the Application of New Advanced Control Technology", Henzel, D.S., and Ellison, W., Proceedings: 1990 SO₂ Control Symposium Volume 1, page 3B-27.
3. "Guidance for Coal Ash Use: Codes and Standards Activities for High Volume Applications," Tyson, S. Proceedings of the 9th Annual International Pittsburgh Coal Conference, October, 1992.