Report Title: Advanced Byproduct Recovery: Direct Catalytic Reduction of SO_2 to Elemental Sulfur

Type of Report: Final

Reporting Period Start Date: September, 1995

Reporting Period End Date: November, 1997

Principal Author: Robert S. Weber

Issue Date: May, 1999

DOE Award Number: DE-AC-95PC95252--09

Submitting Organization:
Arthur D. Little, Inc.
20 Acorn Park
Cambridge, MA 02140

Subcontractor:
Tufts University
Medford, MA 02155

Submitted to
U. S. Department of Energy
626 Cochrans Mill Road
Pittsburgh, PA 15236-0940

Disclaimer

Abstract

Arthur D. Little, Inc., together with its commercialization partner, Engelhard Corporation, and its university partner Tufts, investigated a single-step process for direct, catalytic reduction of sulfur dioxide from regenerable flue gas desulfurization processes to the more valuable elemental sulfur by-product. This development built on recently demonstrated SO_2-reduction catalyst performance at Tufts University on a DOE-sponsored program and is, in principle, applicable to processing of regenerator off-gases from all regenerable SO_2-control processes. In this program, laboratory-scale catalyst optimization work at Tufts was combined with supported catalyst formulation work at Engelhard, bench-scale supported catalyst testing at Arthur D. Little and market assessments, also by Arthur D. Little. Objectives included identification and performance evaluation of a catalyst which is robust and flexible with regard to choice of reducing gas. The catalyst formulation was improved significantly over the course of this work owing to the identification of a number of underlying phenomena that tended to reduce catalyst selectivity. The most promising catalysts discovered in the bench-scale tests at Tufts were transformed into monolith-supported catalysts at Engelhard. These catalyst samples were tested at larger scale at Arthur D. Little, where the laboratory-scale results were confirmed, namely that the catalysts do effectively reduce sulfur dioxide to elemental sulfur when operated under appropriate levels of conversion and in conditions that do not contain too much water or hydrogen. Ways to overcome those limitations were suggested by the laboratory results. Nonetheless, at the end of Phase I, the catalysts did not exhibit the very stringent levels of activity or selectivity that would have permitted ready scale-up to pilot or commercial operation. Therefore, we chose not to pursue Phase II of this work which would have included further bench-scale testing, scale-up, pilot-scale (0.5 MW_e) testing at conditions representative of various regenerable SO_2-control systems, preparation of a commercial process design, and development of a utility-scale demonstration plan.

Table of Contents

List of Figures

List of Figures

List of Tables

Executive Summary

Arthur D. Little, Inc., together with its commercialization partner, Engelhard Corporation, and its university partner Tufts, investigated a single-step process for direct, catalytic reduction of sulfur dioxide from regenerable flue gas desulfurization processes to the more valuable elemental sulfur by-product. This development built on recently demonstrated SO_2-reduction catalyst performance at Tufts University on a DOE-sponsored program and is, in principle, applicable to processing of regenerator off-gases from all regenerable SO_2-control processes.

Both the Federal government and private industry have invested significant resources in the development of advanced, high efficiency, regenerable flue gas desulfurization (FGD) processes, such as NOXSO, the Wellman-Lord process, the magnesium oxide process, the DOE copper oxide process, and the Dow Regenerable Process. These processes generally have a higher SO_2 removal efficiency than conventional FGD systems; often also remove NO_x with high efficiency; and produce little or no waste for landfill disposal. A total of 19 million tons of conventional FGD by-product were produced and landfilled in 1990. However, commercial implementations of these regenerable SO_2-control technologies have generally included a complex and costly liquid Claus plant for processing the regenerator off-gases and generating sulfuric acid. Sulfur dioxide-rich regenerator off-gases must first be partly reduced to produce a mixture of H_2S and SO_2 as a feedstock for the Claus plant. Lack of a simple, cost-effective by-product generation step has hampered commercialization of these advanced high-efficiency processes.

The technology we investigated promised to provide a simple, single-step, cost-effective solution to this problem: elemental sulfur produced from the regenerator off-gas by catalytic reaction with a reducing gas. The commercial embodiment of the proposed technology promised reduced capital and operating costs of regenerable FGD systems, permitting greater and more rapid market penetration; reduced production, transportation and disposal of FGD wastes; and improved SO_2 and NO_x control due to increased use of advanced regenerable emissions control systems. In addition, the proposed technology would generate elemental sulfur as a by-product, rather than sulfuric acid. Elemental sulfur is a higher-value, preferred by-product for which there is a growing world market.

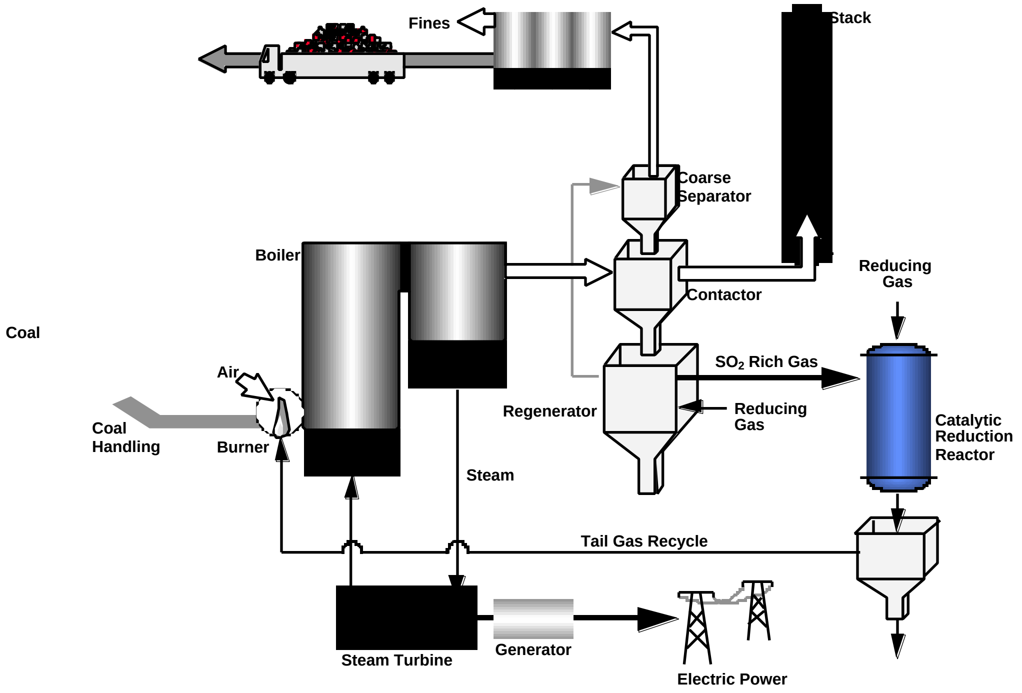
In this program, laboratory-scale catalyst optimization work at Tufts was combined with supported catalyst formulation work at Engelhard, bench-scale supported catalyst testing at Arthur D. Little and market assessments, also by Arthur D. Little. Objectives included identification and performance evaluation of a catalyst which is robust and flexible with regard to choice of reducing gas. The catalyst formulation was improved significantly over the course of this work owing to the identification of a number of underlying phenomena that adversely affected catalyst selectivity. The most promising catalysts discovered in the bench-scale tests at Tufts were transformed into monolith-supported catalysts at Engelhard. These catalyst samples were tested at larger scale at Arthur D. Little, where the laboratory-scale results were confirmed, namely that the catalysts do effectively reduce sulfur dioxide to elemental sulfur when operated under appropriate levels of conversion and in conditions that do not contain too much water or hydrogen. Ways to overcome those limitations were suggested by the laboratory results. Nonetheless, at the end of Phase I, the catalysts did not exhibit the very stringent levels of activity or selectivity that would have permitted ready scale-up to pilot or commercial operation. Therefore, we chose not to pursue Phase II of this work which would have included further bench-scale testing, scale-up, pilot-scale (0.5 MW_e) testing at conditions representative of various regenerable SO_2-control systems, preparation of a commercial process design, and development, in conjunction with a selected electric utility company, of a utility-scale demonstration plan.

Introduction

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 below (Figure 1).

Figure 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.

Description of Byproduct Recovery System

The team of Arthur D. Little, Tufts University and Engelhard Corporation conducted Phase I of the originally envisioned four and a half year, two-phase effort. We sought 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 suggested that the catalyst had the potential for flexibility with regard to the composition of the reducing gas, making it attractive for utility use. 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.

In previous DOE-supported work,[Liu, 1994 #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 showed 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.

Research and Development Activity

The overall objective of this program was to 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 was 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).

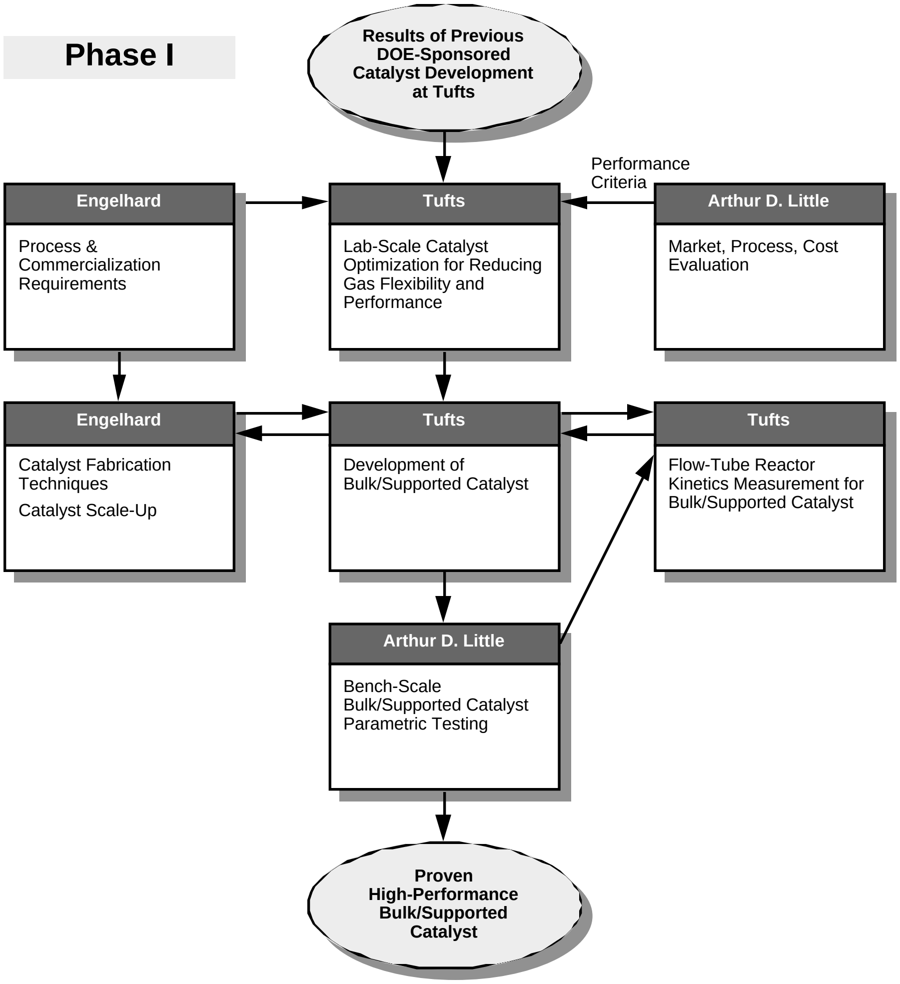
In order to achieve this goal, we devised a structured program including:

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

A description of the methods of investigation that were employed or planned for these program elements is described below (Figure 2)

Market, Process and Cost Evaluation. Information was gathered from public sources and discussions with electric utilities and developers of regenerable sorbent system 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 this information, key performance criteria for the system were defined. The performance and cost of the proposed catalytic process were evaluated and compared to these criteria. In addition, these performance criteria were used to define milestones and to focus catalyst and process development.

Figure 2: Work Elements of this program



Lab-scale Catalyst Preparation/Optimization Studies. Catalyst were prepared using a variety of methods (such as co-precipitation, sol-gel technique) from two candidate fluorite oxides (CeO_2, ZrO_2), four candidate transition metals (Cu, Co, Ni, Mo) and dopants (e.g, La). These catalyst materials were 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 were collected in order to determine the key underlying reaction mechanisms. Parametric tests were performed to 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 were used and catalyst characterization was used to identify active compositions.

Lab-scale, Bulk/Supported Catalyst Kinetic Studies. The best-performing catalysts were appropriately supported on a honeycomb monolith. Small quantities of the supported catalysts were 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 were tested in a bench-scale flow tube reactor at Arthur D. Little. Parametric tests were conducted to assess the influence of temperature, inlet SO_2 concentration, space velocity, and choice of reducing gas on performance. Limited cyclic and duration testing was conducted at this scale.

Utility Review. A utility review team was assembled, consisting of experts from utilities that have experience with regenerable desulfurization technologies or that were considering their application in the near future.

Results and Discussion

Market, Process and Cost Evaluation

This task was performed at Arthur D. Little and was designed 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; and to determine the extent to which application of the advanced byproduct recovery process improves the competitiveness of regenerable sorbent systems.

A survey was conducted to develop a compendium of: 1) flue gas desulfurization (FGD) technologies capable of producing enriched streams of recovered SO_2; and, 2) processes capable of converting the recovered SO_2 to elemental sulfur. The survey focused on identifying those processes that have achieved commercial application; that have attained an advanced stage of development (typically successful prototype testing), whether still actively being pursued or not; or, that are currently under active development at a level beyond laboratory scale. The purpose was of the survey was twofold. First, to establish the database for the range of potential feedstream conditions and most probable, or preferred, reducing gases. Second, to develop the background information for assessing the market potential for one-step SO_2-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.

Survey Results

At the risk of oversimplification, advanced FGD technologies producing an enriched SO_2 byproduct stream generally fall into four major groups, although most of these have subgroups that further differentiate general process approaches (Table 1):

- ***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 SO_2 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 1. FGD Technology and Status Summary

Technology	Developer and/or Current Supplier	Sorption				Regeneration	SO_2 Conversion	Application Focus			Development Status	
		Sorbent	SO_2	H_2S	NO_x			Steam Boilers	IGCC	Process Offgas	Current Status	Extent of Development
Aqueous Metal/Alkali												
MagOx	PECO/Raytheon; Kawasaki; Mitsui/GEESI	$Mg(OH)_2/MgSO_3$	●	---	---	Direct-Fired Thermal	Decoupled	●	---	---	Passive	C: Utility (Acid)-US;Europe;Japan
Wellman-Lord	Davy Environmental	Na_2SO_3	●	---	---	Thermal (Indirect Steam)	Decoupled	○	---	●	Inactive	C: Utility (Acid)-US;Europe C: Refinery (Claus)-Global
ELSORB	Elkem	Sodium Phosphates	●	---	---	Thermal (Indirect Steam)	Decoupled	○	---	●	Active	C: Refinery (Claus)-Europe P: Utility-Europe
ACP	Rockwell/ABB	Na_2CO_3	●	---	---	Molten Bath Reduction	Coupled (Coke)	●	---	---	Abandoned	D: Utility-Abandoned
SOXAL	Allied-Signal (Aquatech)	Na_2SO_3	●	---	---	Electrodialysis	Decoupled	●	---	---	Active	P: Utility-US
SULF-X	PENSYS/DOE	Iron Sulfides	●	---	●	Thermal (Indirect Coal)	Coupled	●	---	---	Inactive	D: Utility-Abandoned
Aqueous Ammonia												
Cominco	Cominco/Olin-Mathieson	Ammonia	●	---	---	Acidification/Stripping	Decoupled	○	---	● ✓	Inactive	C: Smelter; Chemical (Acid)-US
ABS	TVA	Ammonia	●	---	---	Acidulation/Stripping/Thermal	Decoupled	●	---	---	Abandoned	P
Catalytic/IFP/CEC	Catalytic/IFP/CEC	Ammonia	●	---	○	Acidulation/Stripping/Thermal	Decoupled/Liquid Claus	●	---	---	Passive	D: Utility (Catalytic/IFP)-Europe P: (CEC NO_x portion)-Japan
Amine-Based Scrubbing												
DMA	ASARCO	Dimethylaniline	●	---	---	Thermal (Indirect Steam)	Decoupled	---	---	●	Inactive	C: Smelters (Acid/Liquid SO_2)
CANSOLV	Union Carbide	Triethanolamine	●	---	---	Thermal (Indirect Steam)	Decoupled	●	---	●	Inactive	P: Absorption/Regeneration only
Dow Process	Dow Chemical	Proprietary Amine	●	---	○	Thermal (Indirect Steam)	Decoupled	●	---	●	Inactive	P: Absorption/Regeneration only
Sollnox		Polyethylene Glycol	●	---	---	Thermal (Indirect Steam)	Decoupled				Inactive	
NOSOX	Monsanto	Ethanolamine Glut.	●	---	---	Thermal (Indirect Steam)	Decoupled	○	---	●	Inactive	P
Citrate-Based Scrubbing												
Stauffer	Bureau of Mines/Stauffer	Sodium Citrate	●	---	---	Liquid Phase	Coupled	○	---	●	Abandoned	C: Refinery-Abandoned
Pfizer	Bureau of Mines/Pfizer	Potassium Citrate	●	---	---	Liquid Phase	Coupled	○	---	●	Abandoned	P
Zinc-Based Adsorbents												
HGD	General Electric	Zinc Ferrite	●	●	---	Dilute oxygen	Decoupled	---	●	---	Active	P
DSRP	DOE(METC)/RTI	Zinc Titanate	●	●	---	Dilute oxygen	Decoupled	---	●	---	Active	L
ELSE	Amoco		●	●	---	Dilute oxygen	Decoupled	---	---	●	Active	P
Z-Sorb	Phillips	ZnO (Ni-Promoted)	●	●	---	Dilute oxygen	Decoupled	---	●	---	Active	P
Other Metal Adsorbents												
Copper Oxide	DOE(PETC)/TECO	CuO/Alumina	●	---	●	H_2 or Methane	Decoupled	●	---	---	Active	D: Utility-US
Alkali-Based Adsorbents												
Sorbtech	Sorbtech	MgO/Vermiculite	●	---	●	Thermal (Reducing Atm.) Thermal (Oxidizing Atm.)	Decoupled	●	---	---	Active	D: Utility-US
NOXSO	NOXSO	Na_2CO_3/Alumina	●	---	●	H_2,CO(Methane)+Steam	Decoupled (Claus)	●	---	---	Active	D: Utility-US
Physical Adsorption												
Bergbau-Forschung	Mitsui/Uhde/GEESI	Activated Char	●	---	○	Carbon	Decoupled (RESOX®)	●	---	---	Active	C: Utility (Acid)-Germany;Japan
EPDC	EPDC/Sumitomo	Activated Char	●	---	●	Carbon	Decoupled	●	---	---	Active	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 2. FGD Process conditions

Technology	Developer (Current Supplier)	Regeneration	Pretreatment	Product Gas Conditions						
				T(C)	Composition (mol %)					Other Constituents
					SO_2	H_2S	CO_2	H_2O	N_2	
Aqueous Metal/Alkali										
MagOx	PECO/Raytheon; Kawasaki	Direct Thermal (Fluid Bed or Kiln) - Oxidizing	Solids Removal	360±20	15±2	---	15±2	20±4	Balance	SO_3(Trace),O_2(~1%)
	Mitsui/GEESI	Direct Thermal (Fluid Bed or Kiln) - Reducing	Solids Removal	360±20	16±2	---	14±2	20±4	Balance	COS(Trace), CO(~1%)
Wellman-Lord	Davy Environmental	Thermal (Indirect Steam)	Condensed	25±5	92±6	---	Trace	Balance	Trace	SO_3(Trace),O_2(Trace)
ELSORB	Elkem	Thermal (Indirect Steam)	Condensed	25±5	92±6	---	Trace	Balance	Trace	SO_3(Trace),O_2(Trace)
ACP	Rockwell/ABB	Molten Bath Reduction with Coke	NA	NA	---	---	---	---	---	---
SOXAL	Allied-Signal (Aquatech)	Electrodialysis	None							
SULF-X	PENSYS/DOE	Indirect Thermal (Coal)	None	NA	---	---	---	---	---	---
Aqueous Ammonia			Condensed	25±5	92±6	---	Trace	Balance	Trace	SO_3(Trace),NH_3(Trace)
Cominco	Cominco/Olin-Mathieson	Acidification (H_2SO_4)/Steam Stripping								
ABS	TVA	Acidulation/Steam Stripping								
Catalytic/IFP/CEC	Catalytic/IFP/CEC	Acidulation/Steam Stripping + Liquid Claus (IFP)								
Organic-Based Scrubbing		Thermal Stripping (Indirect Steam)	Condensed	25±5	92±6	---	Trace	Balance	Trace	SO_3(Trace),O_2(Trace)
DMA	ASARCO									
CANSOLV	Union Carbide									
Dow Process	Dow Chemical									
Solinox										
NOSOX	Monsanto									
Citrate-Based Scrubbing		H_2 with Liquid Claus	NA	NA	---	---	---	---	---	---
Stauffer	Bureau of Mines/Stauffer									
Pfizer	Bureau of Mines/Pfizer									
Zinc-Based Adsorbents		Dilute oxygen	None	750±20	1-2	---	Trace	---	Balance	Trace O_2, CO, and/or SO
HGD	General Electric									
DSRP	DOE(METC)/RTI									
ELSE	Amoco									
Z-Sorb	Phillips									
Other Metal Adsorbents										
Copper Oxide	DOE(PETC)/TECO	H_2	Condensed	25±5	92±6	Trace	---	Balance	---	
		Methane	Condensed	25±5	60-65	Trace	30-32	2-10	---	Trace CH_4, CO
Alkali-Based Adsorbents										
Sorbtech	Sorbtech	Thermal (Reducing Atm.)	None	750	65±?	30±?	---	Trace	---	S(5%±)?
		Thermal (Oxidizing Atm.-Air)	None	550					Balance	SO_2
NOXSO	NOXSO	H_2	None	640	65±	25±	---	Trace	---	S(10%±)
		Methane	None	640	65±	30±	---	Trace	---	S(5%±)
Physical Adsorption										
Bergbau-Forschung	Mitsui/Uhde/GEESI	Coke/Coal	Condensed	25±5	50-60	---	30-35	Balance	---	Trace SO_x, HCl, HF
EPDC	EPDC/Sumitomo	Coke	None	400	15±	Trace	5±	20±	Balance	Trace NH_3, CO

Table 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	Other
Gas Phase								
Direct Coke/Coal								
RESOX	Foster Wheeler/Uhde/Mitsui?	Coke or Coal	Bergbau-Forschung (Decoupled)	D	Active			
EPDC	EPDC/Sumitomo	Coke			Active			
Outokumpu	Outokumpu	Coal		C: Smelter-Abandoned?	Abandoned			
Reducing Gas								
Allied Chemical	Allied Chemical	Methane or synthesis gas	None	C: Utility(US)-Abandoned	Passive			
Texas Gulf Sulfur	Texas Gulf Sulfur	Methane	None		Passive			
Outokumpu	Outokumpu	Methane or synthesis gas	None	P	Abandoned			
DSRP	DOE(METC)/RTI	?	DSRP (Decoupled)	P	Active			
Parsons FGC	Parsons Process Group	H_2, fed directly into flue gas for catalytic conversion of SO_2 to H_2S	Parsons FGC (Coupled)	P	Inactive			
Sorbtech	Sorbtech	Indirect thermal regen. in reducing atm. (750 C) or in oxidizing atm. (550 C), then to mod. Claus -- proprietary Sorbtech tech. under devel.	Sorbtech Proprietary or Claus	P	Active			
NOXSO	NOXSO	Multi-stage regen. using H_2 or methane to produce H_2S and SO_2 for Claus feed	NOXSO and Claus	D: Utility(US)	Active			
Other								
IFP	Catalytic/IFP/CEC	H_2 with Liquid Claus	Catalytic/IFP/CEC (Decoupled)	D: Utility(Europe)	Passive			
SULF-X	PENSYS/DOE	Indirect calcination of FeS at 700±50 C with some coke	SULF-X (Coupled)	P	Inactive	NA	NA	
ACP	Rockwell/ABB	Molten bath reduction of salts with coke	ACP (Coupled)	D: Utility(US)-Abandoned	Inactive	NA	NA	
Citrate Processes	Bureau of Mines/Stauffer/Pfizer	H_2 with Liquid Claus	Citrate (coupled)	C: Smelter(US)-Abandoned	Inactive			

[1] **Technologies that are potential direct competitors in conversion of enriched SO_2 streams as well as technologies that could compete indirectly by supplanting the need for decoupled gas phase SO_2 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 2 the range of conditions of the byproduct SO_2 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 prioritized the FGD technology groupings to establish a profile of feedstream characteristics most representative of commercialization needs. Consideration was 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 results of this prioritization places technologies into two general categories (Table 3).

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 SO_2 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 appears to be currently stalled.

- Selected aqueous alkali processes - As a group these have not faired 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.

Critical Market Forces

In concert with the development of the technical requirements, we identified critical market forces relative to commercial acceptance of a one-step sulfur conversion technology. This effort was 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 of this project is on utility applications, consideration was also given to other potential markets on an opportunistic basis.

There are a wide variety of FGD technologies being installed around the world on utility power plants and industrial boilers. 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, was to determine what the principal competing FGD technologies would be over the near term (next five years) and the intermediate term (five to fifteen years). We also attempted to forecast where and how sulfur producing technology will fit in. An important aspect was whether a one-step conversion process can play an important role in the competitiveness of producing sulfur from FGD.

Assessment of Short-Term Market

Our assessment of the near-term (5-7 years) market for FGD technologies covered the electric utility industry, the refining and chemical industry, and the ore smelting industry. We recognized that the one-step sulfur recovery technology under development would 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 SO_2 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 SO_2 control.
  - ◊ ***copper smelting*** is moving toward hydrometalurgical technology to process “tailings”.
  - ◊ ***zinc smelting*** is now focused on battery recovery which is not conducive to SO_2 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 SO_2 reduction technology under development is aimed at the next generation of highly-efficient regenerable FGD technologies which have yet to reach the market.

Process simulation

We performed a process evaluation, in which we simulated the process energy balances, temperature requirements, reactor volumes, and recycle rates, for two reducing gas production methods. These analyses were tied to the requirements of utilities and the various regenerable sorbent technologies under development. We prepared 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.

Initial data from experiments conducted at Tufts, wherein methane was used as the reducing agent, indicated the following:

- As temperature is increased, to afford higher conversion of SO_2 to elemental sulfur, production of undesirable species such as H_2S and COS increases.

- While chemical conversion of SO_2 is enhanced by excess reducing agent, production of H_2S and COS outpaces gains in sulfur yield.

Given the need for conversion of SO_2 to S to be upwards of 95%, these results were not encouraging. In discussion it was agreed that testing with carbon monoxide (CO) as the reducing agent should be done, to see whether CO offered enhanced prospects for conversion.

High conversion and high selectivity could be achieved if tail gas could be recycled. This would imply the need for significant custom engineering to couple the sulfur recovery subsystems with the primary plant equipment, namely the boiler or gasifier, and would likely be characterized by unattractive economics. To clarify this point, we used the process analysis tool we developed for this program to examine the gross implications of recycling the sulfur recovery waste stream. Energy considerations were not a part of this analysis, a significant omission given the practicality of implementing a recycle stream since sulfur condenses at temperatures well below those employed in the direct catalytic reduction process. Still, it was valuable to simply quantify material flows, develop an understanding of the implications insofar as equipment size requirements, and make an assessment as to whether a recycling strategy could be viable. First a baseline case was defined, for both a utility boiler and an IGCC application, based on engineering judgments and expected technology improvements. Then, a sensitivity analysis was conducted to examine the effect of several key design parameters on recycle requirements for the system as a whole. These were as indicated below.

Table 4. Design parameters for estimating sensitivity of DCR process to recyle.

Parameter	**Baseline**	**Sensitivity**
Adsorber efficiency	90%	99%
Adsorber regeneration timescale	0.80%	0.88%
Regenerator gas O_2 concentration (IGCC)	2.0%	5.0%
Increased sulfur yield	60%	95%
Reducing gas stoich. equivs.	2.0%	1.0%

The results are effected strongly by the assumed sulfur cleanup technology. For IGCC, zinc oxide based technology using vitiated air was assumed; for a utility boiler, copper oxide using based technology using methane was assumed. These two technologies have very different requirements regarding regenerant gas volumes, as is indicated quite strongly in the results of the analysis.

IGCC: For the parameter sensitivities considered, mole flow increases associated with recycle were roughly 25-50% over those associated with the corresponding cases involving no recycle. This, even without energy considerations, recycle for this technology configuration must be deemed unacceptable.

Boilers: For the parameter sensitivities considered, mole flow increases associated with recycle were roughly 0.5-1.0% over those associated with the corresponding cases involving no recycle. Recycle for this technology appears tenable on the basis of economics for *new* plants. No ready conclusions could be made for the retrofit market.

Subsequently we adapted our process analysis tool to enable calculations regarding process economics. In particular it was of interest to quantify effective deratings associated with the tapping of carbon monoxide from the syngas stream produced in IGCC. Additionally it was of interest to develop a technology cost target based on competing technologies, i.e. lime-based desulfurization and Claus plant sulfur recovery.

An attempt was made to estimate reducing gas costs, which appear to dominate the capital and operating costs.

In IGCC, syngas produced in the process can be used as the reducing agent for sulfur recovery. Taking a coal sulfur content of 3% on a mass basis, a stoichiometric amount of reducing gas represents a requirement of approximately 4% of the syngas produced. We made the following assumptions:

- Base plant capacity of 500 MW

- Base plant installed cost of $1,500/kW
- Cost-capacity scaling exponent of 0.6

The installed cost of the base plant was assumed to be $750 Million. The cost of an oversized plant which could divert 4% of product for the sulfur recovery function, would be :

$$\text{Cost (Oversize)} = \text{Cost (Base)} * ((500/0.96) / 500)^{0.6} = \$750\text{ MM} / 0.96^{0.6} = \$769\text{ MM}$$

suggesting a capital equipment investment for reducing gas supply of on the order of $20 Million. At an annual capacity factor of 70%, the IGCC facility would produce 3.1 Billion kilowatt-hours a year. If the reducing gas supply equipment were to be capitalized over ten years, this would correspond to a charge increment to consumers of 0.07 cents/kWh, or about 1% of typical electricity prices in the US. The annual cost of the equipment would be about $2 Million.

The cost of coal required to generate the requisite amounts of syngas represents the predominant operating cost. Using a coal cost of $1.30/MMBtu, these operating costs amount to approximately $44/ton of sulfur recovered. In a 500 MW plant running on coal with a 3% sulfur content, approximately 30.5 kilotons of sulfur would be recovered each year. The cost of coal associated with reducing gas requirements is approximately $1.4 Million.

The total costs of reducing agents associated with sulfur recovery appears to be on the order of $3-4 Million/year.

Previously it had been thought that natural gas would be the preferred reducing gas. However, in light of the Tufts data, it did not appear that methane was sufficient for producing sulfur yields consistent with the economic requirements for the technology. If it could be used, and if natural gas were available at $2.50/MMBtu, the cost per unit of sulfur recovered would be roughly $47/ton. That cost is comparable to the current market price of sulfur. We did not attempt to estimate the effects on the price of sulfur owing either to the startup of a regenerable flue gas technology or to the increasing availability of sulfur as refineries incorporate higher levels of hydrodesulfurization to limit the amount of sulfur in the fuels they produce.

For a 500 MW power plant, running on coal with a 3% sulfur content, about 37.5 kilotons of sulfur would be recovered annually. The associated cost of natural gas would be on the order of $1.8 Million. Auxiliary equipment would include flow delivery and control systems, and would add some expense. The total reducing gas cost would thus be about $2.0 Million/year.

Laboratory-scale catalyst testing and optimization

This task was carried out by Tufts University, to optimize catalyst composition and preparation method for use with a variety of reducing gas compositions and qualities, including syn-gas and natural gas. Under four subtasks, Tufts prepared and characterized the catalysts, conducted adsorption/desorption studies, measured catalytic activity in a packed-bed microreactor, and conducted parametric tests and kinetic measurements. Specifically, Tufts optimized 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 were 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) were examined as promoters to obtain a catalyst composition active in various reducing gases. The fluorite oxides used in this work were ceria (CeO_2) and zirconia (ZrO_2).

Catalyst Preparation and Characterization Tufts prepared 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) were also examined.

Catalysts were routinely 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 were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry. Selected active catalysts were 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 were evaluated in adsorption/desorption studies with CO, COS, and SO_2 to determine the reaction mechanism. These experiments led to an understanding of the low selectivity of this catalyst to the undesirable byproduct COS and facilitated catalyst optimization. A thermo-gravimetric analyzer, coupled with a residual gas analyzer, were used for these tests.

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

(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 acquired using methane and wet synthesis gases covered the range of possible regeneration gases available. It was not necessary to test dry synthesis gases since the tests with CO and methane provided information on ideal performance without water. For each reacting gas mixture, the reactor temperature was increased and then reduced to establish light-off and fall-off behavior of each catalyst. Elemental sulfur yield, catalyst activity and catalyst selectivity were used to identify the most promising catalysts.

Parametric Studies and Kinetic Measurements After identifying promising catalysts, an extensive parametric study was carried out to provide reactor design information. The parametric studies addressed the effects of water vapor and/or carbon dioxide on catalyst activity and elemental sulfur yield as well as the effect of reducing gas composition (H_2/CO ratios/CH_4) on catalyst activity and sulfur yield.

The parametric studies were 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 were in the range 50 to 700°C. A kinetic model was developed from the data obtained at short contact time (< 0.1g s/cc) in a small diameter catalytic reactor. This included the effects of H_2O and CO_2 on the specific activity.

Work at Tufts University focused on screening tests of a variety of catalyst formulations. The catalyst preparation technique used consisted 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 were then filtered, washed twice with hot deionized water, dried overnight, and then calcined in air at 650°C for 3 hr.

Previously reported results have indicated that:

> Ni-Ce(La)-O catalysts show the highest activity, even at relatively low Ni concentrations (2%).
>
> 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.
>
> Low metal contents are necessary to avoid agglomeration and sintering of the metal oxides at high temperatures.
>
> Use of synthesis gas as the reducing agent can shift the catalyst light-off temperatures back to the values previously reported for pure CO.

Most of the bulk catalysts used in this work were prepared by a gelation/precipitation using metal nitrates and urea[4]. This method provides well-dispersed and homogeneous mixed metal oxides. The preparation process consists of the following steps: 1) mixing nitrate salts of metals with urea and heating the solution to 100ºC under continuous stirring; 2) after coprecipitation, boiling the resulting gels of Ce or Zr vigorously for 8 h with continually addition of makeup water. 3) filtering and washing the precipitate twice with hot deionized water; 4) drying the precipitate overnight in a vacuum oven at 110ºC; 5) crushing the dried lumps into smaller particles and calcining in static air for a few hours at 650ºC. The typical surface area of CeO_2 catalysts prepared in this manner was higher than 70-120 m^2/g. However, the surface area of CeO_2 and La-Ce-O catalysts was not stable even after 750 °C calcination, and the typical surface area after reaction up to 750 °C was around 35 m^2/g (Table 5). The samples used for the SO_2 and CH_4 reactions were further heated at 720ºC for 3 h. The bulk density of the catalysts was around 2 g/cm^3.

Table 5. Physical Properties and Activity of Ceria and Doped Ceria

Sample	Surf. area of fresh sample (m^2/g)		Surf. area of used sample[a] after reaction at 750 °C		Activity of Sample (T=700 °C)	
	650 °C calcination	750 °C calcination	dry	wet	X-SO_2	Y-[S]
CeO_2	75	40	29 (20)	33	0.255	0.255
4.5%La-Ce-O	90	59	33		0.221	0.211
10%La-Ce-O	106	64	37		0.236	0.226
20%La-Ce-O	120	58	34 (30)	28	0.299	0.291
30%La-Ce-O	78	59	35		0.206	0.198
Cu/La/CeO_2 (1/1/98wt%)[b]	87	<69				

a) all catalysts were pre-reduced (at 600 °C in 10% CO/He for 1 hr). The values in parenthesis are the surface area of the samples calcined at 750 °C.
b) Prepared by Engelhard using an impregnation method.

All catalysts were tested in a laboratory-scale, quartz tube packed bed flow reactor with a porous quartz frit supporting the catalyst, which was in powder form. A 0.5 in. O.D. x 18.5 in. long bed was used in catalyst tests. The experiments were carried out under nearly atmospheric pressure. A cold trap connected at the outlet of the reactor was used to separate and collect the elemental sulfur and water from the product stream. The product gas was analyzed by a HP5880A Gas Chromatograph (GC) with a Thermal Conductivity Detector(TCD). A 1/4 in. O.D. x 6 in. long packed glass column of Chromosil 310 was used in the GC to detect CO, CO_2, COS, SO_2 ,CS_2 and H_2S.

The results are shown in terms of sulfur dioxide conversion, X-SO_2, and elemental sulfur yield, Y-[S], defined as follows:

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

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

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:

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

When pre-reduction was used, the fresh catalysts were pre-reduced by heating for one hour in 9.9% CO/He at 600 °C. After activation, a gas mixture of SO_2 -CH_4 -He was introduced into the reactor and the temperature was raised from 400°C to 750°C in steps of 50 -100 °C. Water was injected into the heated gas line with a calibrated syringe pump. One or two temperatures were typically checked in the fall-off mode for hysteresis phenomena as well as potential catalyst deactivation. A gas mixture with a molar ratio of $SO_2 / CH_4 = 2$ was used in the work reported here. The mole percent of SO_2 in the feed gas was typically unity. The contact time was 0.36g·s/cc (NTP), and space velocity varied for different catalysts depending on the catalyst density.

Figure 3 shows the experimental activity data for SO_2 reduction by CH_4 on the bulk CeO_2 catalyst and La-Ce-O catalysts. The pre-reduction of catalyst in 10% CO / He at 600 °C was not effective for CeO_2, and CeO_2 without pre-reduction showed the highest SO_2 conversion, implying that surface oxygen species participates in activating methane. This is in agreement with the literature [5][Trovarelli, 1996 #5] which suggests that the activation of methane occurs through surface lattice oxygen and surface coordinatively unsaturated (cus) oxygen. The pre-reduction of CeO_2 inhibited the adsorption of methane due to the lack of available cus oxygen and surface oxygen species. However, the selectivity of non-pre-reduced CeO_2 was lower than that of the pre-reduced one due to higher H_2S and COS formation.

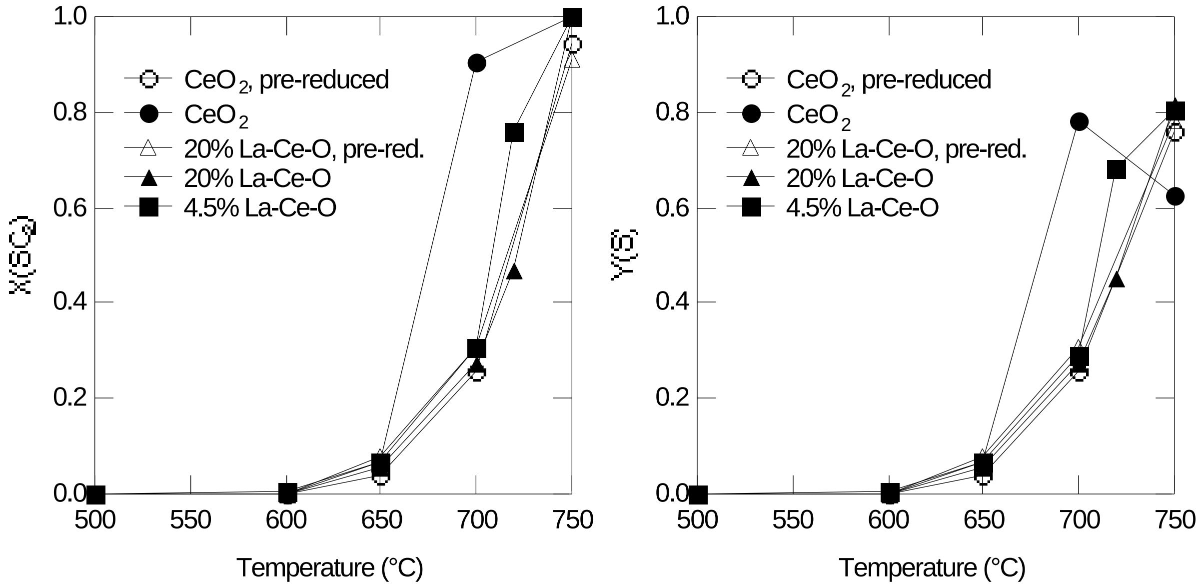


Figure 3. Effect of pre-reduction on the activity of CeO_2 (La). Reaction conditions: 1% SO_2, 0.5% CH_4, balance He, 0.36 g s/cm^3.

For 4.5%La-Ce-O catalyst, the pre-reduction slightly improved the activity of the catalyst, while for 20%La-Ce-O catalyst, the pre-reduction had negligible effect. Both of these catalysts were less active than CeO_2. Under reaction conditions, the catalysts surface is partially sulfated, and SO_3 may be formed by reaction with the surface oxygen and making it more difficult to be reduced. At any rate CH_4 and SO_2 may be competing for the surface oxygen. The existence of oxygen vacancies at the lower temperature may not be desirable, as it can not activate CH_4 in the presence of strongly bound SO_2. The pre-reduction effect on the activity of CeO_2 and La-Ce-O catalysts also indicates that the reduction of SO_2 by methane follows a different mechanism from the SO_2 reduction by CO, which is believed to be redox mechanism.[Liu, 1995 #6]

The introduction of water vapor in the reacting atmosphere may affect the catalytic activity by adsorption of H_2O on the catalyst surface. Figure 4 shows that by adding 12% water vapor, more than 80% and 60% SO_2 conversion of CeO_2 was lost at 700°C and 750°C, respectively, when compared to the dry condition. The activity could be recovered by removing water vapor from the reacting gas, as illustrated in Figure 5. At 720°C, by removing the water vapor from the feed gas, SO_2 conversion was increased from 0.2 to 0.8 within 30 minutes.

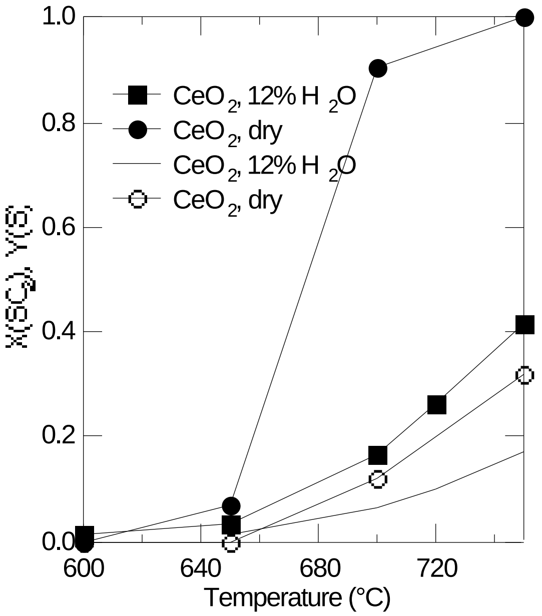


Figure 4. Effect of adding water on the activity of CeO_2. Samples were calcined at 650°C. Reaction conditions: 1% SO_2, 0.5% CH_4, 12% H_2O, contact time = 0.36 g s/cm^3.

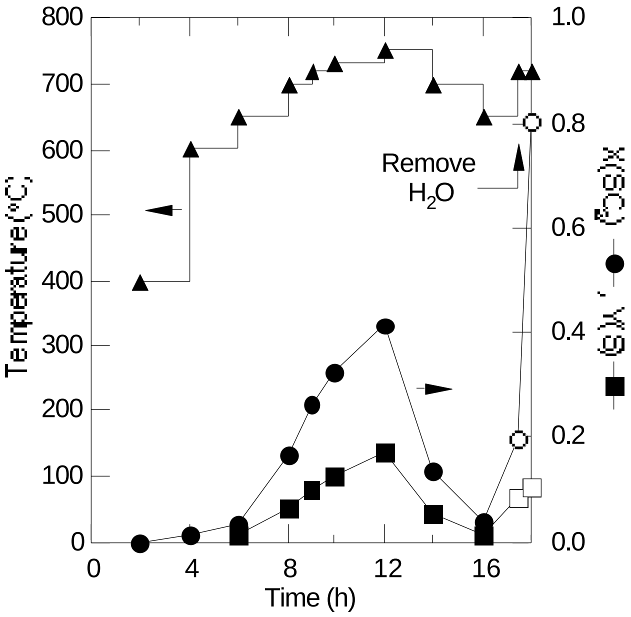


Figure 5. Demonstration of the recovery in the activity of CeO_2 when water is removed from the feed stream. Conditions for the first 17 hours were the same as those in Figure 4.

The effect of water at high concentrations, such as might be observed during transients in the operation of a large scale unit, were investigated using the standard protocol described above. The catalysts consisted of both CeO_2 and La-promoted CeO_2, containing 5 or 10% Ni. The concentration of water was set at either 10vol% or 40vol% of the feed, using a pump and hot block. The reducing agent was CO in all of these studies since, by itself, it produces no H_2S (and only trace quanties of COS under these conditions). For the rare earths alone, adding water strongly decreased the overall conversion at temperatures below about 500°C (Figure 6a). At higher temperatures, some of the activity was regained but the selectivity changed to produce significant quantities of H_2S (Figure 6b).

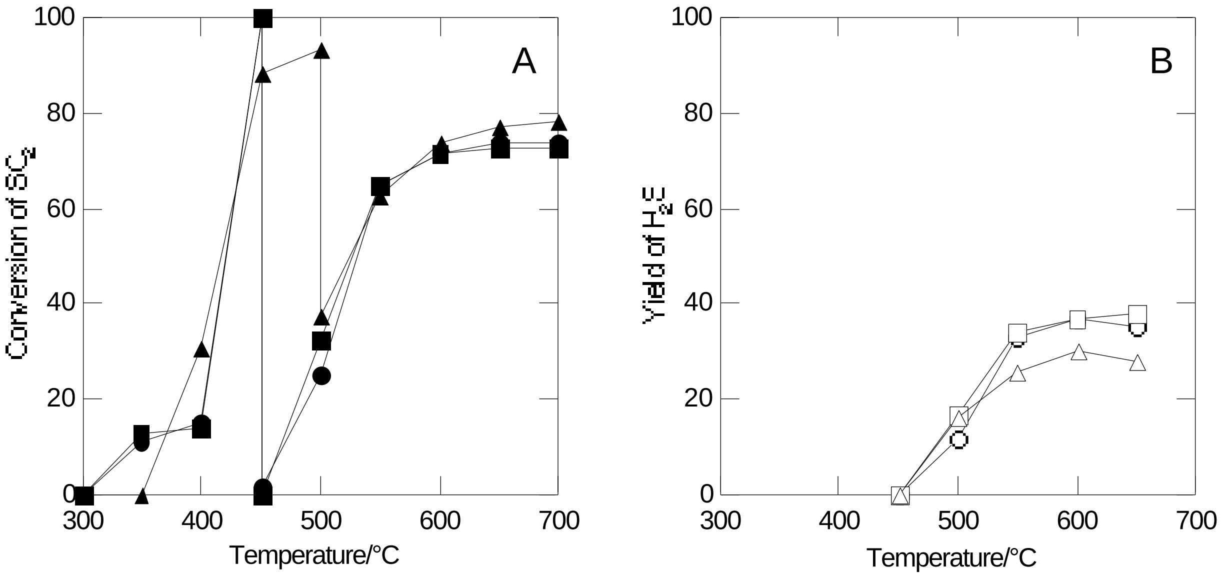


Figure 6. Reduction of 1.05% SO_2 by CO over ceria and promoted ceria with and without adding 10% water (at either 450°C or 500°C as indicated by the arrows). Contact time = 0.11 g s/cm^3, CO/SO_2=1.5 to 1.6. Catalysts: ●—$Ce(10\%Zr)O_2$; ■— $Ce(10\%La)O_2$;▲—CeO_2. Filled symbols represent conversion of SO_2; open symbols represent yield to H_2S..

The effect of adding water is reversible, over at least 8 hours of continuous addition (Figure 7).

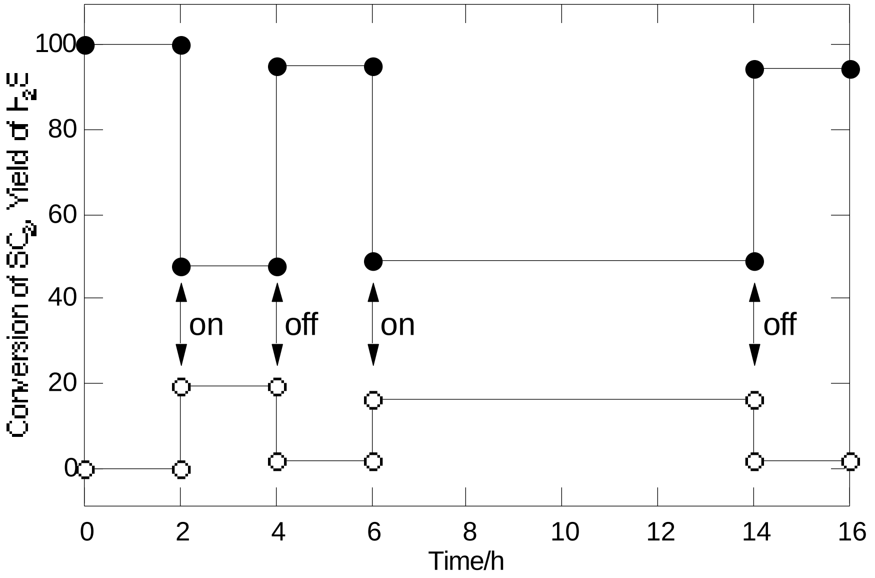


Figure 7. Reduction of 1.1% SO_2 by CO over $Ce(10\%Zr)O_2$ at 500°C. Conditions: contact time = 0.11 g s/cm^3, CO/SO_2=1.51. At the indicated times, 10% water was added or removed from the inlet stream. Filled symbols represent conversion of SO_2; open symbols represent yield to H_2S..

The Ni-containing catalysts maintained a significant level of activity in the presence of water (Figures 8a,b) but still produced substantial quantities of H_2S, albeit at longer contact times. It should be noted, however, that the results shown in Figure 8 represent very severe conditions with respect to water.

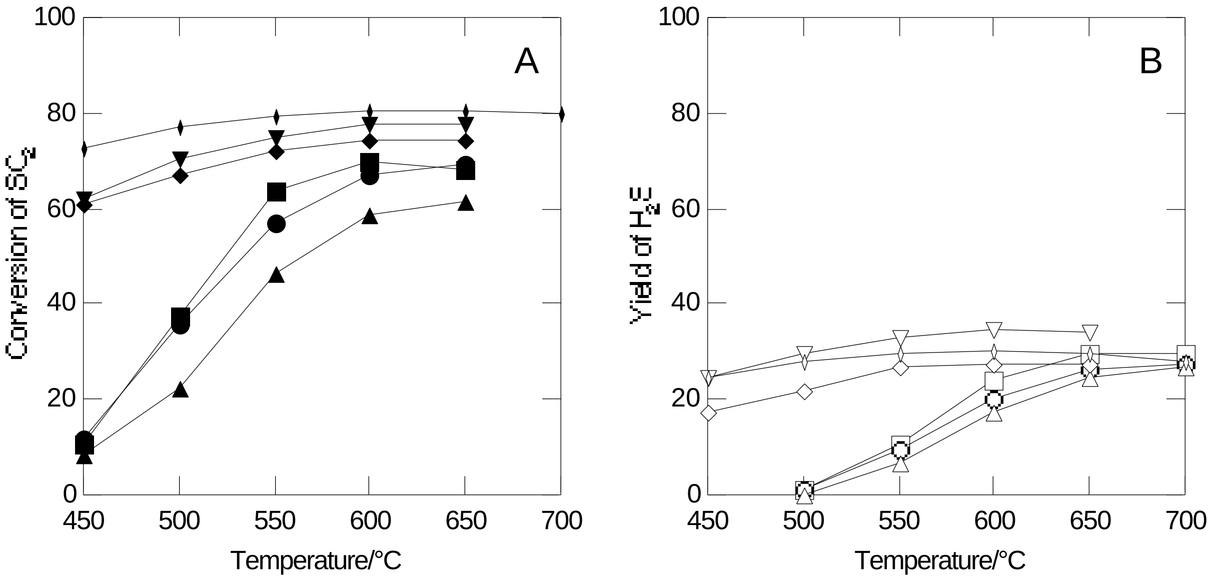


Figure 8. Reduction of 1.05% SO_2 by CO in the presence of 10% water. Conditions: contact time = 0.11 g s/cm^3 (except as indicated), CO/SO_2=1.5-1.7. Catalysts: ●—Ce(10%Zr)O_2; ■—Ce(10%La)O_2;▲—CeO_2; ▼—10%Ni[Ce(5%La)O_x] ; ◆—10%Ni[Ce(5%La)O_x] pre-reduced at 600°C in flowing hydrogen; ▮—Ni_y[Ce(La_{1-y})O_x]. Filled symbols represent conversion of SO_2; open symbols represent yield to H_2S.

While the addition of Ni and Cu improved the activity of Ce(La)O_x for SO_2 reduction by CO both in dry and wet gas stream, the addition of Ni and Cu had negligible effect on the activity of Ce(La)O_X catalyst for SO_2 reduction by CH_4. Figure 9 shows that at a contact time of 0.18 g s/cc and SO_2/CH_4 =1, 4.5%La-Ce-O had higher SO_2 conversion than Ni and Cu modified Ce(La)O_X, while the latter two catalysts showed slightly higher selectivity to sulfur. The same result was obtained at higher contact times of 0.36 gs/cc and 0.72 gs/cc. The lack of activity enhancement by the metal modified catalysts may be explained by the fact that the metals only promote the reducibility of ceria at low temperature, whereas high temperature are needed for the methane activation.

The 5%Cu-Ce(La)-O catalysts showed slightly higher selectivity. Figure 10 shows the effect of contact time on 5%Cu-Ce(La)-O catalysts. The activity of the catalyst was increased by increasing the contact time, and the selectivity to sulfur (defined as the ratio of Y-[S]/X-SO_2) was decreased when the contact time increased from 0.18 to 1.2 gs/cm^3. This was consistent with the previous result of Ni-Ce(La)-O catalyst, implying that elemental sulfur is the primary product in the SO_2 reduction by CH_4, while H_2S and COS, if formed, are secondary products.

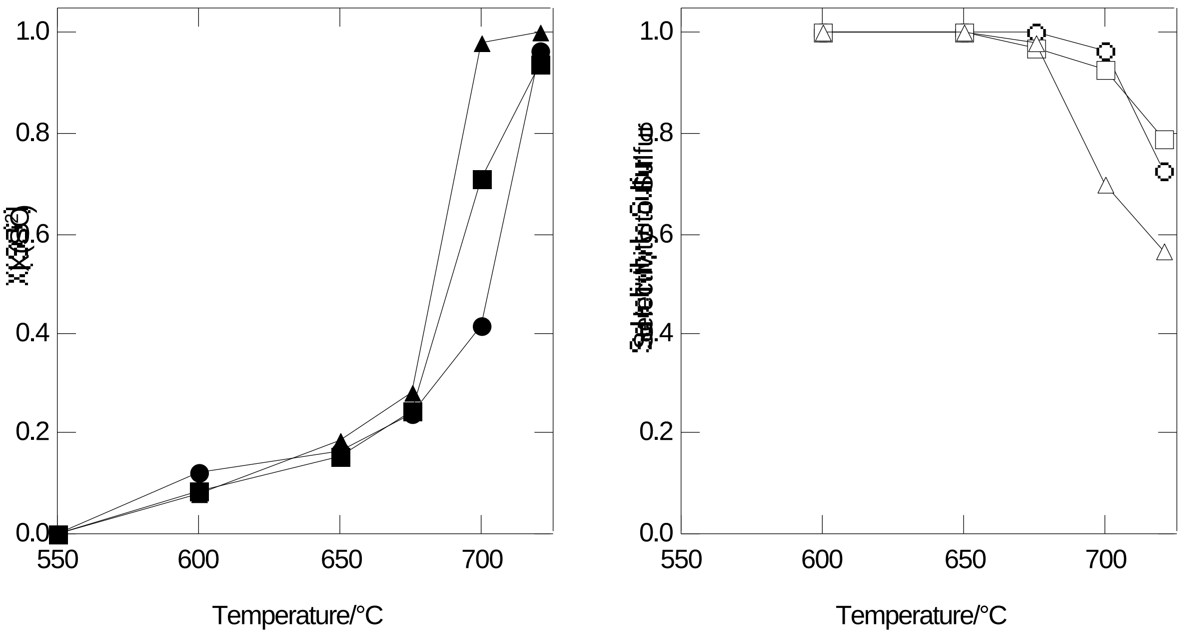


Figure 9. Effect of catalysts composition on SO_2 reduction by CH4. Catalysts: ● - 5%Ni-Ce(La)-O; ■: 5%Cu-Ce(La)-O; ▲: 4.5%La-Ce-O. Conditions: 1%SO_2-1%CH_4-balance He, contact time 0.18 gs/cm^3. Filled symbols represent conversion of SO_2; open symbols represent yield to H_2S.

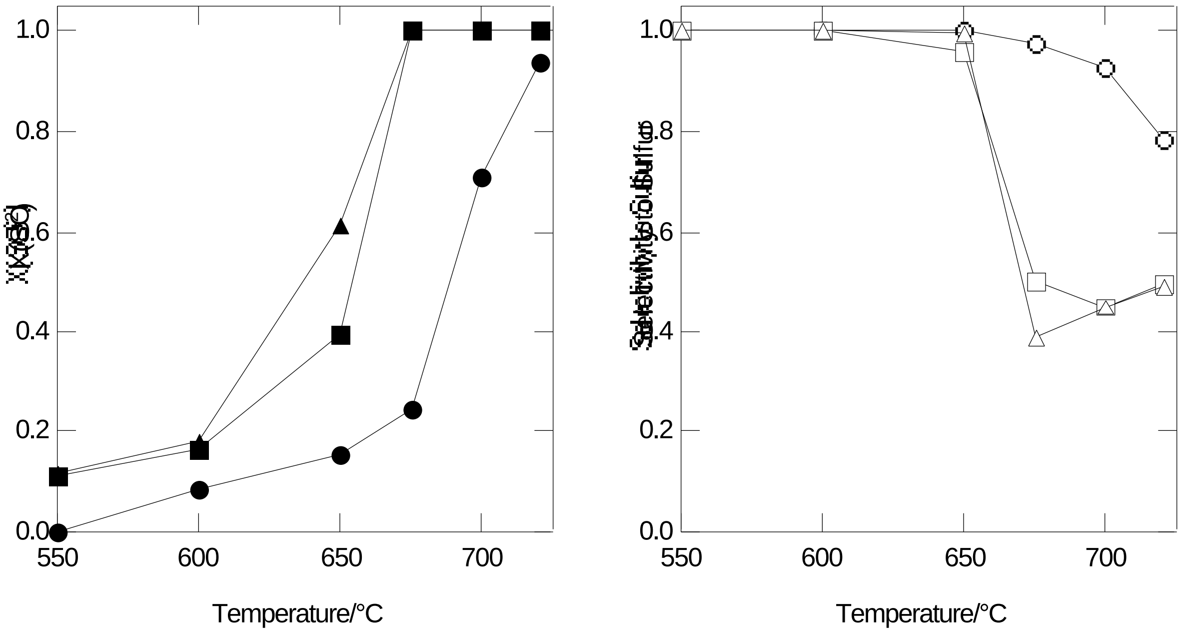


Figure 10. Effect of contact time on SO_2 reduction by CH_4. Catalyst: 5%Cu-Ce(La)-O. Conditions: 1%SO_2-1%CH_4-balance He, contact time ●: 0.18 gs/cc, ■: 0.72 gs/cc and ▲: 1.2 gs/cm^3. Filled symbols represent conversion of SO_2; open symbols represent yield to H_2S.

The higher the ratio of CH_4 to SO_2, the higher the activity and the lower the selectivity of the catalysts, as shown in Figure 11. Interestingly, the results indicated that the reaction had a positive dependence on methane, therefore by using excess methane we could lower the reaction temperature, keeping both high activity and selectivity. This is a very important finding for developing a process with maximum activity and selectivity.

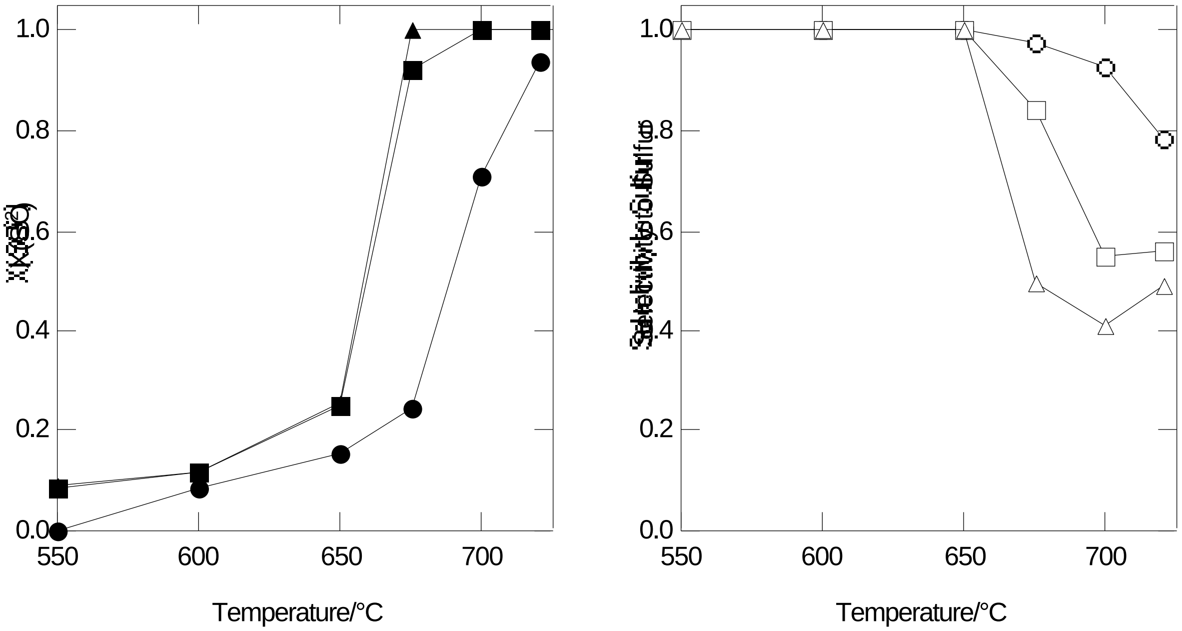


Figure 11. Effect of CH_4/SO_2 ratio on SO_2 reduction by CH4. Catalyst: 5%Cu-Ce(La)-O. Conditions: 1%SO_2, contact time 0.18 gs/cm^3, CH_4/SO_2: ● - 1; ■ -2; ▲ - 3. Filled symbols represent conversion of SO_2; open symbols represent yield to H_2S.

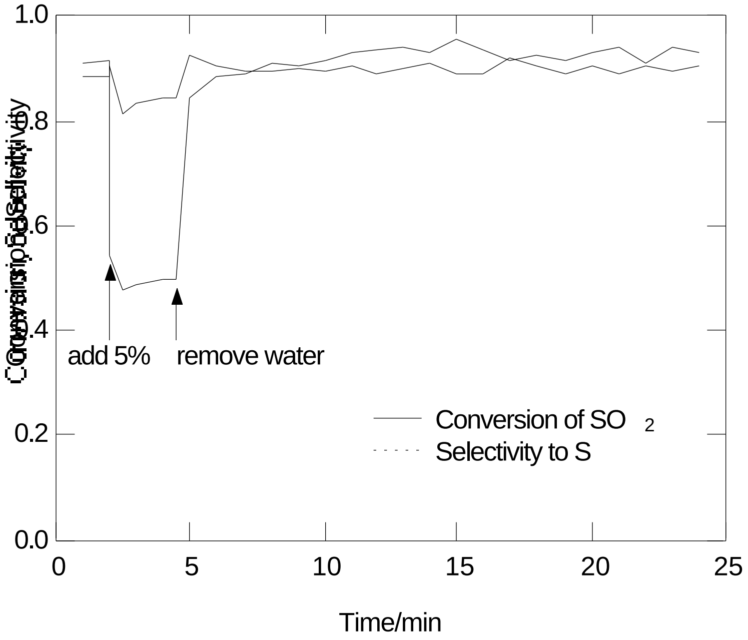


Figure 12. Effect of water on SO_2 reduction by CH_4. Conditions: 1%SO_2-2%CH_4-He, contact time 0.18 gs/cm^3.

The activity was decreased when 5%H_2O was added into the feed stream as indicated in Figure 12. However, the selectivity was still high and almost all the SO_2 was converted to sulfur. The activity of the catalyst could be recovered when water was removed from the feed stream and no aging effect was observed during a 20-hr long test.

One of the possible paths for H_2S formation during SO_2 reduction by CH_4, is via the H_2 produced by methane pyrolysis:

$$CH_4 \rightarrow 2H_2 + C$$

Hydrogen may then attack the adsorbed sulfur to form H_2S. As described above, by operating at low temperature, we can prevent methane pyrolysis (i.e. H_2 formation) and maximize sulfur yield. Hydrogen as a reductant is also of interest for the direct reduction of SO_2 to elemental sulfur. Therefore, the reduction of SO_2 by H_2 was studied on Ce(La)O_X and metal modified ceria catalysts. Ce(La)O_X was found to be an active catalyst and the light-off behavior was similar to that for SO_2 reduction by CO, as shown in Figure 13. The performance of this catalyst could be explained by the redox model in which CO is simply replaced by H_2 as the reductant. However, the light-off temperature was inferior to CO, in that a higher temperature was required.

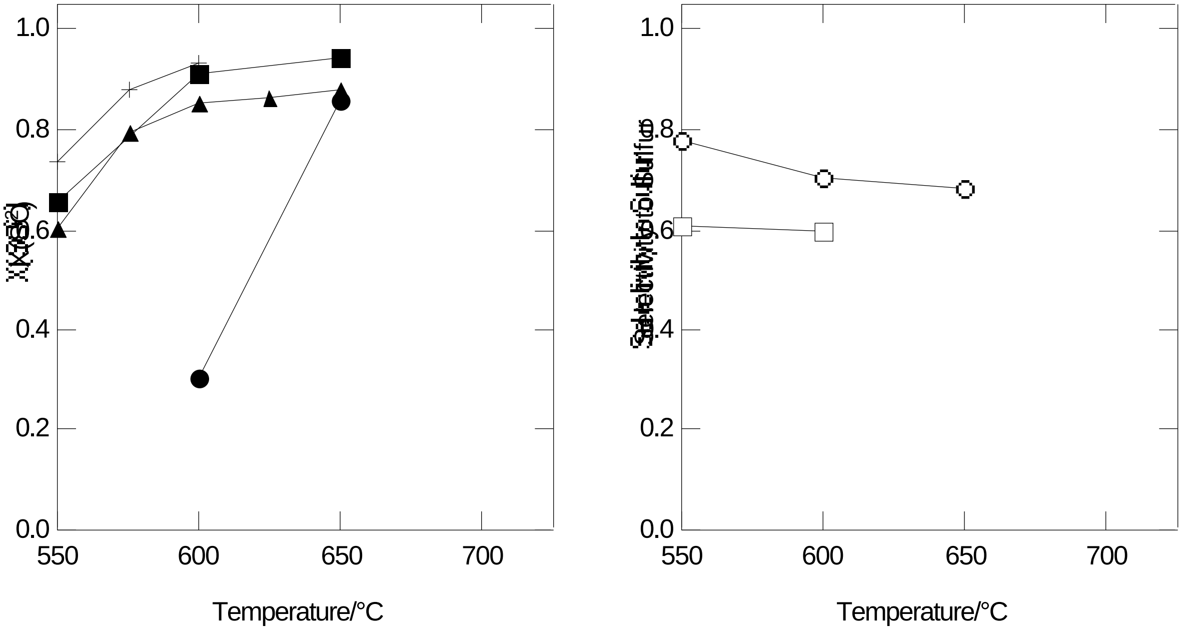


Figure 13. Effect of metal on the reduction of SO_2 by H_2: activity of Ce(La)O_x. Catalysts: ● - 4.5%La-Ce-O; ■ 5%Fe-Ce(La)-O; ▲: 5%Cu-Ce(La)-O; ◆: 5% Ni-Ce(La)-O. Conditions: 1%SO_2-2%H_2-He, contact time 0.18 gs/cm^3. Filled symbols represent conversion of SO_2; open symbols represent yield to H_2S.

By adding 5% Cu, Ni or Fe into Ce(La)O_x catalyst, the light-off temperature was decreased by about 100 °C (Figure 13). However, the presence of H_2 promotes the production of H_2S, and the highest sulfur yield obtained was 64% when feed gas stream contained 1%SO_2 and 2%H_2 at a contact time of 0.18 gs/cm^3 (~40,000 h^{-1}).

It is clear from Liu's thesis work[6] on SO_2 reduction by CO that the activity of Cu-Ce(La)-O was not sensitive to metal content. The reducibility of catalysts, i.e., the oxygen vacancy and oxygen mobility, which was the key for the reaction of SO_2 and CO, was not affected by metal content. However, in the case of the H_2+SO_2 reaction, a positive effect of the incorporation of iron was identified. Figure 14 shows that the SO_2 conversion and sulfur yield of Fe-Ce(La)-O catalysts was enhanced by the addition of more iron. More experiments with high content of metal are necessary to pursue the effect of metal content on the activity and selectivity of the catalysts.

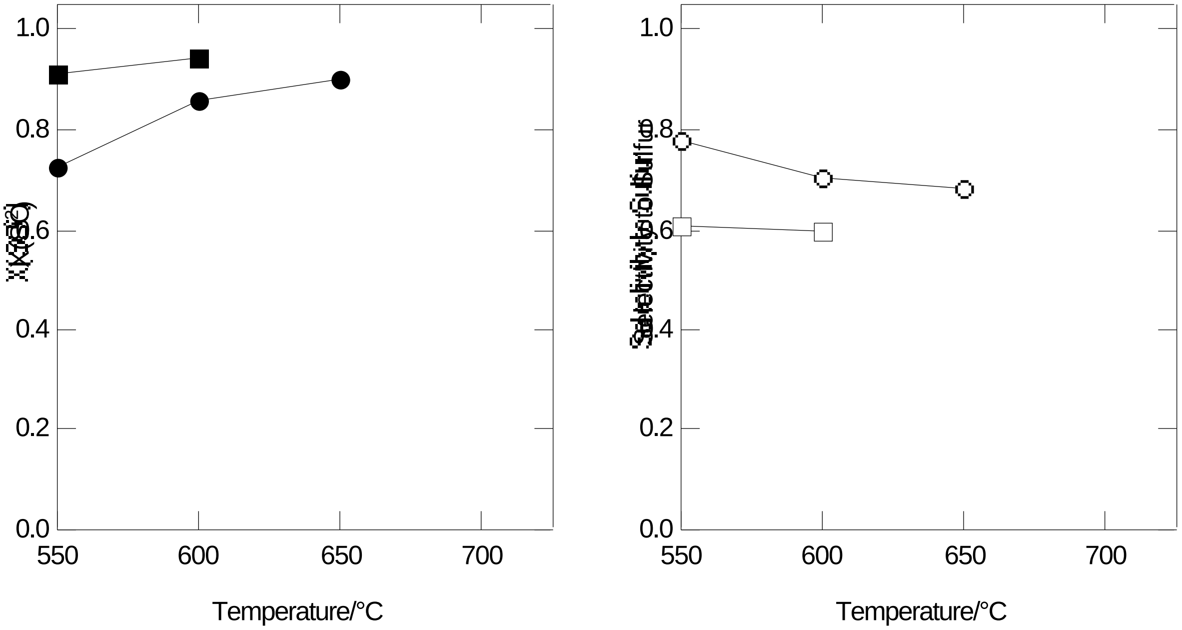


Figure 14. Effect of metal content on the reduction of SO_2 by H_2. Catalysts: ● - 15% Fe-Ce(La)-O; ■: 5%Fe-Ce(La)-O. Conditions: 1% SO_2, 2% H_2, balance He, contact time 0.18 gs/cm^3. Filled symbols represent conversion of SO_2; open symbols represent yield to H_2S.

Preparation of monolith-supported catalysts

Engelhard worked closely with Tufts and Arthur D. Little to specify the appropriate catalyst structures to meet the engineering requirements for the targeted sulfur recovery systems. In particular, they prepared supported catalysts in the form of honeycombs for bench-scale testing and they provided guidance regarding the establishment of activity and simulated aging tests to quickly and efficiently determine performance characteristics of catalyst formulations. They also were prepared to assist in estimating the costs of materials and manufacture of the catalysts which proved to have sufficient performance.

The catalysts were prepared by washcoating techniques so as to contain the component elements and other properties identified by the experiments at Tufts (confirmed by x-ray fluorescence and BET surface area measurements). The washcoat material was tested at Tufts to confirm its activity and selectivity. We relied on Engelhard to specify the appropriate loading of catalyst, to prepare them with radial and axial uniformity and to select the appropriate support. They selected cordierite monoliths in the form of right cylinders, approximately 4 cm in diameter and 6 cm tall, with a cell density of 400 per square inch (62 cells/cm^2) and a catalyst loading of 1-2 g/in^3 (0.06-0.12 g/cm^3). The excellent agreement in performance between the powdered catalysts prepared at Tufts and tested in the laboratory-scale reactors with the monolith-supported catalysts tested in the bench-scale reactor at Arthur D. Little, attests to the judgement and skills of the Engelhard team.

The reaction kinetics over a Cu/La/CeO2 catalyst prepared by Engelhard were measured at Tufts. In particular, the effect of varying the SO_2 concentration at a fixed ratio $CH_4/SO_2 = 0.5$ was determined. The rate data were fit by a first order rate equation, $r = k P^n(SO_2)$. The resulting rate constant was a weak funciton of the partial pressure of SO_2, with the value of n varying between 0.06 to –0.265. The rate constant varied with temperature according to the relation:

$$k = 1.352 \text{ x } 10^6 \exp(-205.9\text{x}10^3/RT)$$

i.e., the apparent activation energy was about 206 kJ/mol, which is higher than the activation energy for SO_2 reduction by CO over similar catalysts (75-85 kJ/mol) [7]

Bench-scale testing

Arthur D. Little designed and fabricated a bench-scale SO_2 reduction reactor facility to conduct bench-scale, parametric tests to evaluate the performance of the monolith-supported catalysts (Figure 15). Gases simulating a regenerator off-gas stream and the reducer gas stream were metered by mass flow controllers. Water vapor was supplied from a steam generator whose exit flow rate was monitored by measuring the pressure drop across a calibrated orifice plate. The steam was superheated to prevent condensation. All the inlet lines were heat traced by inline heaters or heating tape as appropriate. The catalytic reduction reactor was approximately 2 liters in volume and was constructed of a nickel alloy steel to prevent corrosion by the wet, acid inlet stream.

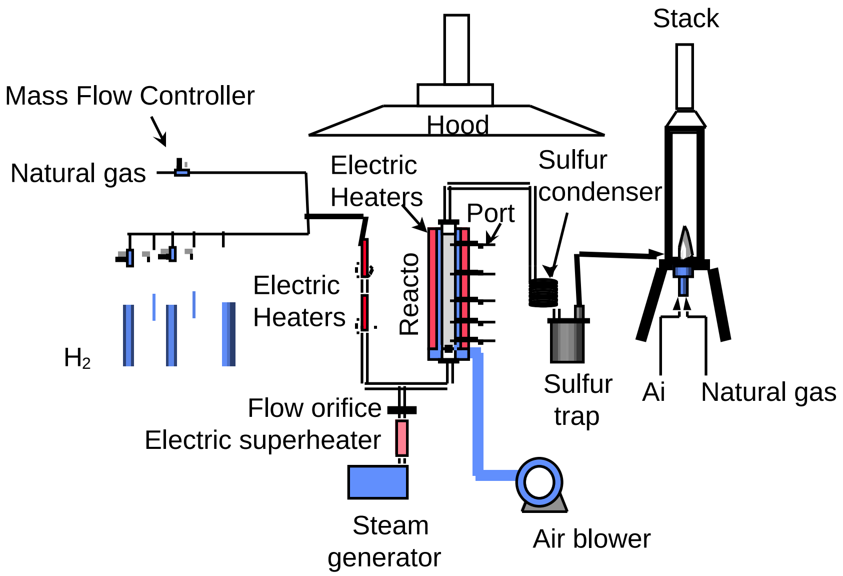


Figure 15. Schematic of the bench-scale flow rig.

The reactor itself is shown schematically in Figure 16. It is approximately 2 in internal diameter and 4 ft long.. It was equipped with 6 sampling ports and thermocouple ports along its length. A heat exchanger was located downstream of the reactor to condense sulfur that formed during the reaction. The sulfur was collected in a pot located below the heat exchanger. The tail gas was fed to a natural-gas fired afterburner to flare any remaining reducing agents and to convert any toxic, reduced sulfur species (H_2S, COS) into sulfur oxides.

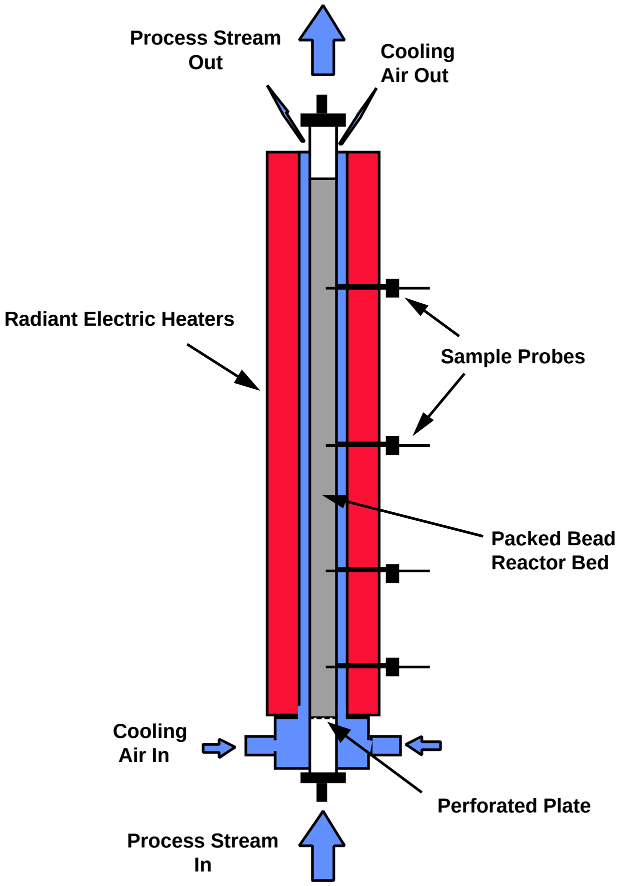


Figure 16 Schematic Diagram of Bench-Scale Catalytic Reactor

The inlet and outlet compositions were monitored using online analyzers for CO, CO_2, SO_2 and hydrocarbons (flame ionization detector) (Figure 17). All sulfur was condensed and separated from the sample stream. The samples were then filtered and diluted with clean, dry air and further dried using a membrane separator. The clean, dry, S-free sample was then analyzed using two continuous ultraviolet SO_2 analyzers, one of which was equipped with a total sulfur oxidizer. which oxidized any reduced sulfur species and permitted them to be quantified. Bag samples were taken for periodic off-line analysis by gas chromatograph. Operation of the rig (temperatures, gas flows, afterburner status) was monitored continuously by a suitably equipped computer and environmental gas detectors (H_2, CO), which would shut down the flows and heaters in the case of an unsafe situation.

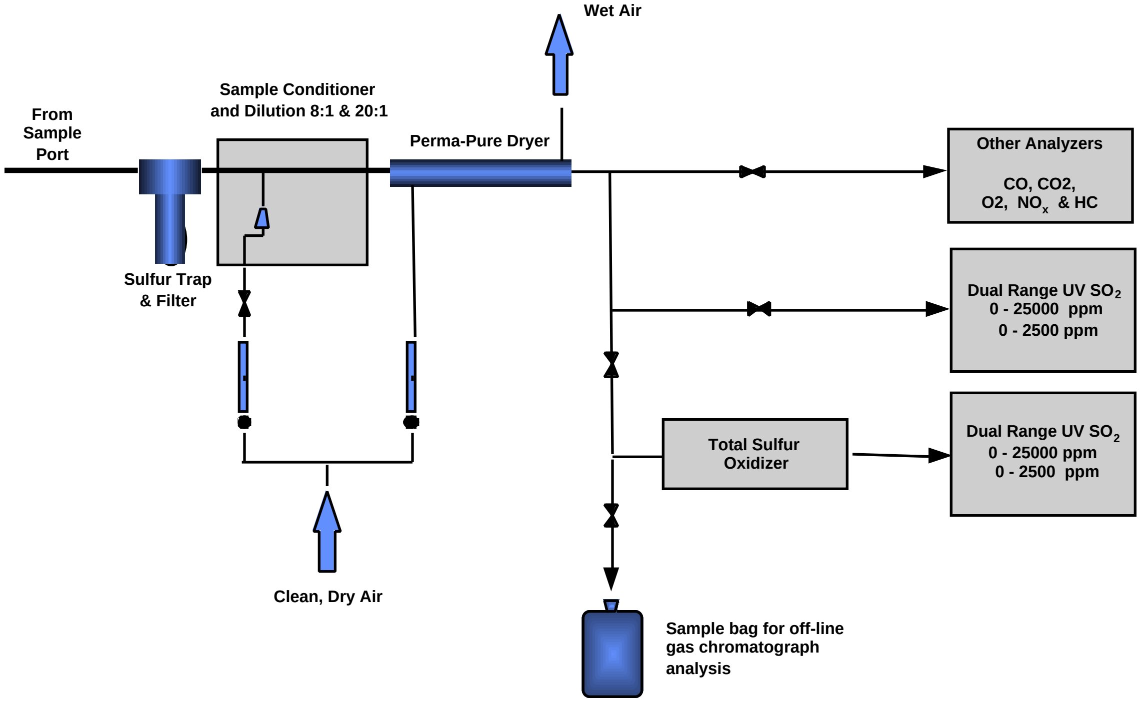


Figure 17 Gas Sampling and Conditioning System

The rig was constructed to handle temperatures as a high as 1000ºC and sized to handle gas flow rates equivalent to space velocities as high as 100,000 h^{-1} which corresponds to a nominal flow rate of 100 slpm. Depending on the regenerable FGD process being simulated, this flow rate would be equivalent to 10 - 100 kW_e of power generation capacity. The rig was designed to deal with the range of gas compositions characterisitic of two types of FGD processes, namely, those based on ZnO and those based on CuO (Table 6).

Table 6. Compostions of flue gas from two regenerable FGD systems

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	SO_2 1.3% H_2S - CO_2 Trace CO Trace H_2O - O_2 Trace SO_3 Trace N_2 98.7%	**Regeneration with** **H_2 CH_4** SO_2 92% 63% H_2S Trace Trace CO_2 - 30% CO - Trace H_2O 8% 7% O_2 - - SO_3 - - N_2 - -

We performed bench-scale tests using the catalyst materials that had 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. Discussions with our colleagues at Tufts focused the experimental plan to include just those sets of catalysts and test conditions that likely would meet the design goals of the overall conversion process using CO, synthesis gas or methane as the reducing agent, both with and without water. The monolith catalyst contained 1% CuO supported on CeO_2, prepared at Engelhard according to the typical precipitation recipe developed at Tufts. The surface area of the washcoat composition was 209 m^2/g as measured by multipoint BET. The composition of the catalyst layer (XRF) was 0.52wt% CuO, 96.7wt% CeO_2, with traces of ZrO_2, La_2O_3 and Pr_2O_3. The cordierite monoliths were 1.75 inches in diameter (1 inch = 2.54 cm), their cell density was 400 cells/in^2, and the catalyst loading was approximately 1.7 g/in^3. The reactor was charged with four 3-inch monolith segments, to give a total charge of about 50 g of the Cu-Ce-O.

The reduction of SO_2 with CO, with CH_4 and with synthesis gas was carried out using this catalyst over a range of contact times and temperatures that spanned those employed by the group at Tufts. The summary results (Table 7) were strikingly similar to those obtained at Tufts, confirming the activity of the catalyst in both CO and methane as well as its sensitivity to hydrogen and water. The catalysts exhibited no significant degradation in behavior over day-length runs that were repeated over two weeks of operation.

Table 7. Reduction of SO_2 using a monolith catalyst.

Reactants	Temperature/°C	Contact time /g s/cm^3	Conv. of SO_2	Sel. to S
1% SO_2, 2% CO	500	0.1	0.90	0.96
1% SO_2, 2% CO, 3% H_2O	500	0.1	0.76	0.42
	600	0.1	0.74	0.54
1% SO_2, 2% CH_4	675	0.1	0.77	0.81
1% SO_2, 2% CH_4, 3% H_2O	675	0.1	0.44	0.84
1% SO_2, 1% CO, 3% H_2	525	0.17	0.95	0.24
	600	0.17	0.97	0.00

Operation of this larger scale reactor reinforced a practical detail that would attend a commercial scale system. It is apparent that the catalyst must effect the desired conversion in a single pass since separation of the sulfur requires cooling of the effluent stream, which would then need to be reheated if it were to be recycled. This consideration was not accounted in the process analysis described above because it became apparent only at the end of the program. It places a great constraint on the activity and selectivity of the catalyst and was a significant factor in our decision not to pursue further scale-up of the catalyst without a great more development in the laboratory.

Had the results at larger scale been more promising we would have refined the 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 by revisiting leading architect/engineering companies, regenerable sorbent system developers, industry consultants and EPRI. Then, based on those interviews we would have defined the key performance criteria for the system and estimated the potential market for advanced, catalytic reduction of SO_2 to elemental sulfur in utility and industrial applications. Similarly, in anticipation of commercially viable performance of the catalyst system, we assembled a utility review team, consisting experts from utility companies that have experience with regenerable desulfurization technologies or that were considering their application in the near future. The following individuals generously agreed to serve on this industrial review panel to evaluate the technical feasibility and to critique the practical details of implementing a sulfur conversion process based on this catalytic technology:

> Jeri Catherine Penrose of Sargent & Lundy. She is a senior engineer involved with the DOE piloting operation of the CuO clean up system.
>
> Randall Rush, of the Southern Company. He is Director of their advanced coal gasification program and is directing thie demonstration facility at Wilsonville where they will be hosting an RTI technology test.
>
> William Ellison, an independent FGD consultant. Mr. Ellison has been involved in much of the innovative flue gas desulfurization technology in utility and other industries.
>
> Krishna Parmeswaran, of ASARCO. He has more than 20 years of experience in the smelting business.

We did not call upon them to serve in this capacity, however: given the results of the preliminary process simulation and the experimental results at the bench scale, we deemed it prudent to delay those interviews and conversations until we were able to provide performance data from a catalyst system that met the minimum requirements of activity and selectivity. That challenging goal persisted through the program.

Conclusions

Through a combination of experimental and analytical studies we were able to identify and partially address some of the major challenges in the efficient conversion of sulfur oxides from dilute flue gas. Extensive laboratory studies at Tufts University succeeded in greatly improving the performance of the best catalyst formulation known at the beginning of this program. In particular, it was found that La-doped ceria is a highly active catalyst for SO_2 reduction by CH_4. Strong adsorption of SO_2 forms surface sulfate and inhibits methane activation at temperatures below 600°C. The reaction between SO_2 and CH_4 begins ona partially sulfated catalyst. Thus, the light-off temperatures of ceria-based catalysts depend on the thermal stability of the sulfates. The activation of methane may involve surface oxygen species and partially reduced metal oxide sites. Two independent reactions are proposed and have been used in this work to explain the catalytic performance of ceria-based oxides. The addition of transition metals, nickel and copper, affects the selectivity under fuel-rich conditions by catalyzing the complete oxidation of methane. In contrast, nickel provides extra sites for methane dissociation at high temperature and results in low catalyst selectivity to elemental sulfur. In the presence of water vapor, $Ce(La)O_x$ is a poor catalyst. However, the metal-promoted catalysts, especially the $Cu\text{-}Ce(La)O_x$ is still a very good candidate for further development of this class of catalysts for practical applications.

Those results were confirmed at larger scale using monolith-supported catalysts prepared by Engelhard and the bench-scale apparatus constructed and operated at Arthur D. Little. Engelhard was able to translate the catalyst formulation, prepared initially in gram quantities, into larger quantities of a washcoatable formulation that was representative of the microscopic behavior of the Tuft’s catalysts and that could withstand the rigors of bench-scale testing.

Throughout the program, the results of the market and technology assessments were used to focus the experimental work on a suitable set of reducing agents and process conditions. By the end of this program, we recognized that a catalyst system which would meet market needs would necessarily exhibit extraordinarily high, single pass conversion in the presence of hydrogenbearing reducing agents. Moreover, depending on the upstream FGD process, the catalyst system would also have to contend with large levels of inlet sulfur.

Since the catalyst systems we had in hand at the end of the program required improvement to meet those very stringent goals we did not pursue the second phase of the original, overall program. The second phase would have given more opportunity for catalyst development but would also have involved the design and operation of a small scale demonstation unit.

The motivation for this program, namely the potential need by utilities and other operators of SO_2-containing flue gas, still is timely. Therefore, we would like to suggest that fundamental research on this promising catalyst system be continued at the laboratory scale.

References

1.Association, N.C., *Steam Electric Plant Factors*. 1992.
2.Henzel, D.S. and W. Ellison, Proc. 1990 SO_2 Control Symposium, 1990. **1**: p. 3.
3.Tyson, S., Proc. 9th Annual International Pittsburgh Coal Conference, 1992.
4.Matijevic, E. and W.P. Hsu, J. Coll. Interface. Sci., 1987. **118**: p. 506.
5.Trovarelli, A., Catal. Rev. Sci. Tech., 1996. **138**: p. 439.
6.Liu, W., A.F. Sarofim, and M. Flytzani-Stephanopolous, Appl. Catal. B., 1994. **4**: p. 167.
7.Liu, W., . 1995, MIT.