

DOE/PC/95252--T/
~~95013--T/~~

Arthur D Little

**Advanced
Byproduct
Recovery:**

**Direct Catalytic
Reduction of SO₂ to
Elemental Sulfur**

**First Quarterly
Technical Progress
Report**

**Report to
Department of Energy
Pittsburgh Energy Technology
Center
Under Contract #
DE-AC-95PC95252**

February, 1996

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**Karen Benedek
Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts
02140-2390**

**Maria Flytzani-Stephanopoulos
Tufts University
Medford, MA 02155**

Reference 54177

**CLEARED BY
PATENT COUNSEL**

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Table of Contents

1. Introduction	1-1
1.1 Background.....	1-1
1.2 Description of Byproduct Recovery System.....	1-2
1.3 Research and Development Activity.....	1-2
2. Work Breakdown Structure.....	2-1
2.1 Phase I Task 1: Market, Process and Cost Evaluation.....	2-1
2.2 Phase I Task 2: Lab-Scale Catalyst Testing/Optimization.....	2-1
2.3 Phase I Task 3: Catalyst Preparation and Costing	2-4
2.4 Phase I Task 4: Bench-scale Testing.....	2-5
2.5 Phase I Task 5: Utility Review.....	2-6
2.6 Phase I Task 6: Management and Reports	2-6
3. Objectives for First Quarter Activity	3-1
4. First Quarter Technical Progress	4-1
5. Plans for Next Quarter	5-1
5.1 Catalyst Development Work	5-1
5.2 Process Evaluation Work	5-1
6. References.....	6-1

List of Tables

Table 4-1: Precursors used in Catalyst Preparation	4-2
Table 4-2: Total BET Surface Area of Various Mixed Oxide Catalysts	4-4

List of Figures

Figure 1-1: Regenerable Sorbent System.....	1-1
Figure 1-2: Work Elements	1-4
Figure 4-1: XRD Pattern of 15%Cu-Ce(La)-O	4-6
Figure 4-2: XRD Pattern of 15%Co-Ce(La)-O	4-7
Figure 4-3: XRD Pattern of 15%Ni-Ce(La)-O	4-8
Figure 4-4: XRD Pattern of 15%Cu-Zr(Y)-O.....	4-9
Figure 4-5: XRD Pattern of 15%Co-Zr(Y)-O.....	4-10
Figure 4-6: XRD Pattern of 15%Ni-Zr(Y)-O.....	4-11

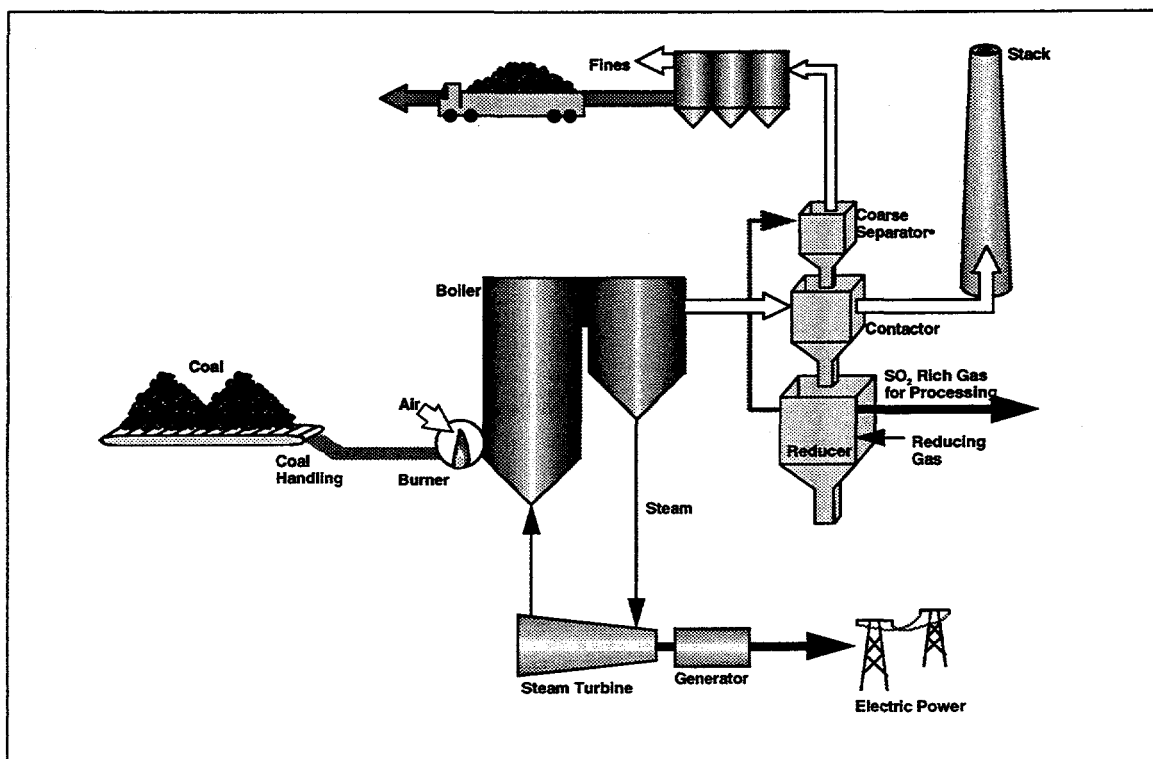
1. Introduction

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 will be 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.

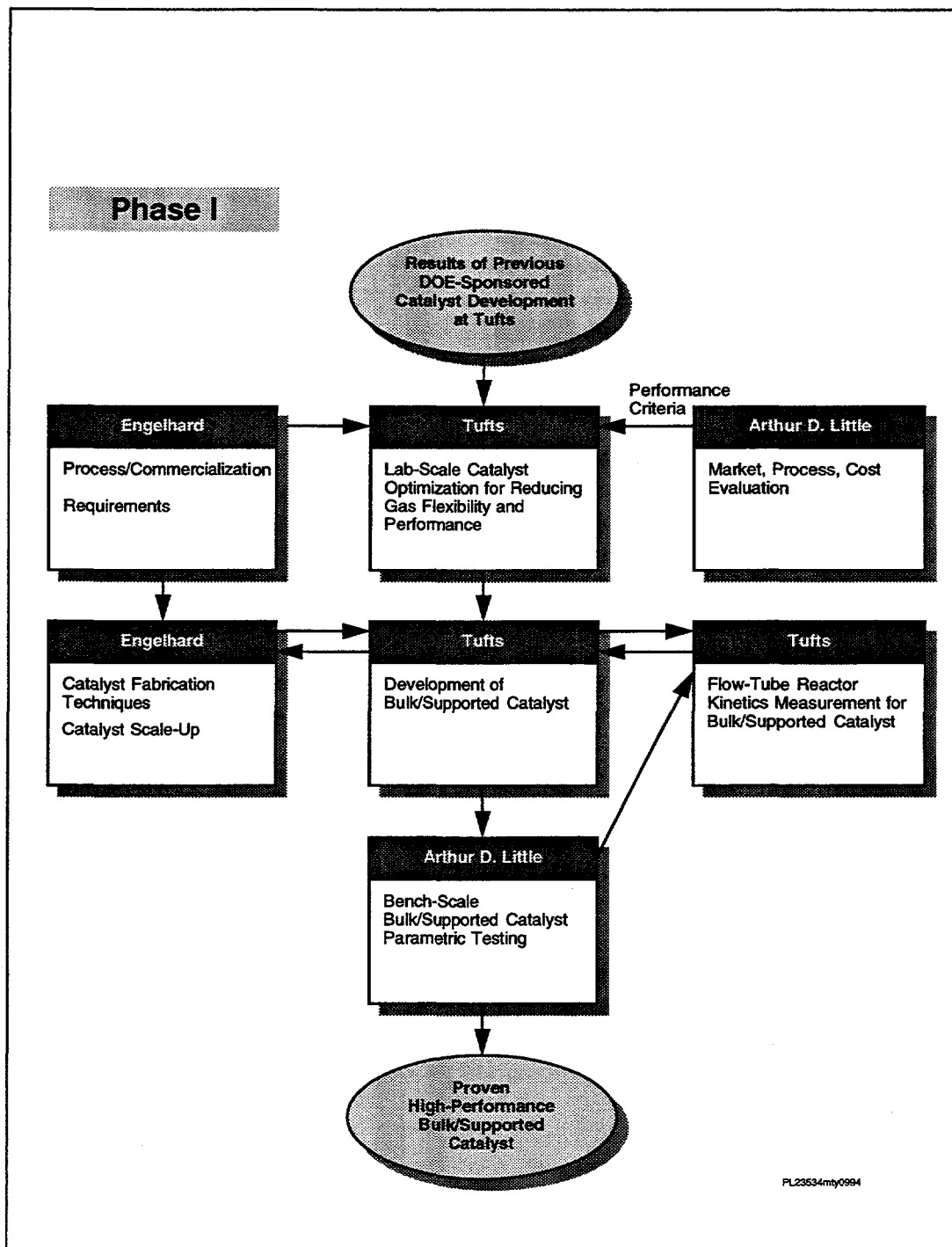
Lab-scale Catalyst Preparation/Optimization Studies. Catalyst will be prepared using a variety of methods (such as co-precipitation, sol-gel technique) from two candidate fluorite oxides (CeO_2 , ZrO_2) and four candidate transition metals (Cu, Co, Ni, Mo). These catalyst materials will be tested at 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 will be conducted by Arthur D. Little. We will interview 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 will prepare 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 will also prepare 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 will be carried out by Tufts University, a subcontractor to ADL. Under four subtasks, Tufts will prepare and characterize the catalysts, conduct adsorption/desorption studies, measure catalytic activity in a packed-bed microreactor, and conduct parametric tests and kinetic measurements. Specifically, Tufts will optimize the catalyst composition and preparation method for use with a variety of reducing gas compositions and qualities, including synthesis gas and natural gas.

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

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

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

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

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

Catalytic Activity Measurements in a Packed-Bed Microreactor Tufts will conduct catalyst activity tests under steady conditions in an existing packed-bed microreactor.

Screening tests will be conducted with a reducing gas consisting of 1% 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. ADL will design, 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 500 cc 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 Niagra 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.

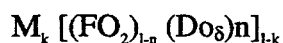
3. Objectives for First Quarter Activity

The objectives for the first quarter were to prepare and characterize transition metal fluorite oxide composite catalysts. These catalysts will later be tested for their SO₂ reduction performance.

4. First Quarter Technical Progress

Catalyst Preparation and Characterization

Transition metal fluorite oxide composite catalysts with the general formula:



are under investigation in this project as catalysts for the reduction of SO_2 to elemental sulfur. In recent work these materials were found to be very active catalysts for the reduction of SO_2 by CO ^{4,7}. Additionally, the same materials are excellent total oxidation catalysts^{5,8-11}. In the above catalyst formulation FO_2 is fluorite oxide (CeO_2 and ZrO_2). CeO_2 and ZrO_2 are providing not only catalyst support but also high oxygen vacancy concentration and oxygen mobility. Oxygen vacancy concentration is further enhanced by the addition of small amounts (less than 5 at.%) of trivalent and divalent dopants, (DO_3) such as La_2O_3 , Gd_2O_3 , Y_2O_3 , MgO , CaO , and SrO . Transition metals M (Cu , Co , Ni) are added into the catalyst to improve the electronic and surface adsorption properties.

Transition metal fluorite oxide composite catalysts were prepared and characterized in terms of surface area and crystal phase composition. During this quarter we followed a variation of our previous coprecipitation technique for synthesizing the mixed oxide catalysts.

The transition metal fluorite oxide catalysts were synthesized by coprecipitating nitrate salts by urea at about 100°C. The precursors used for catalyst synthesis are listed in Table 4-1. The coprecipitation method consisted of the following steps:

1. Nitrate salts (approximately 25 mmol Ce or Zr salts, and desired amount of doping elements) and 24 g of urea (99%, A.C.S. grade, Aldrich) were dissolved in 200 cm³ deionized water. The resulting solution was heated to 100°C and continuously mixed using a magnetic stirrer. Upon heating, the aqueous solution of urea yields ammonium and cyanate ions¹²:



In an acidic solution, cyanate ions react rapidly to give carbon dioxide and ammonium ion:



whereas in neutral and basic solutions, carbonate ions and ammonia are formed

Table 4-1: Precursors used in Catalyst Preparation

Element	Precursor	Source
Ce	ammonium cerium(IV) nitrate, 99+ %	Aldrich
Zr	zirconyl nitrate hydrate, 99.99 %	Aldrich
La	lanthanum nitrate pentahydrate, 99 %	Aldrich
Y	yttrium nitrate pentahydrate, 99.9 %	Aldrich
Gd	gadolinium nitrate, 99.9 %	Johnson Matthey
Ca	calcium nitrate tetrahydrate	Mallinckrodt
Mg	magnesium nitrate hexahydrate	Sigma
Sr	strontium nitrate, A.C.S. grade	Fisher
Cu	copper (II) nitrate hydrate, A.C.S. grade	Johnson Matthey
Ni	nickel (II) nitrate hydrate, A.C.S. grade	Alfa
Co	cobalt (II) nitrate hydrate, A.C.S. grade	Johnson Matthey

2. After coprecipitation, the resulting gels of Ce and Zr were vigorously boiled for 8 hours at 100°C. During boiling, two main processes are taking place: (i) aging of Ce and Zr gels, which is an important step in catalyst preparation influencing final catalyst properties, such as surface area, and (ii) removal of excess urea through the reactions (1) - (3). In addition, during boiling gaseous products of urea decomposition (ammonia and carbon dioxide) are removed, preventing formation of transition metal-ammonia complexes, so that almost complete precipitation is achieved.
3. After aging, the precipitate was filtered, washed twice in boiling deionized water, and dried in a preheated vacuum oven (80-100°C) overnight.
4. Dried samples were crushed and calcined in flowing air typically 650°C for Ce-based catalysts and 500°C for Zr-based catalysts. The heating rate was 5°C/min.

Slow decomposition of urea provides the slow increase of pH necessary for precipitation, which can not be achieved with other precipitating agents, such as ammonium carbonate or aqueous solution of ammonia. In addition, urea decomposition occurs homogeneously in the solution, providing homogeneous precipitation.

This procedure leads to complete precipitation of Cu containing catalyst, whereas Co and Ni were present in the solution even after 8 hours of boiling. For Co and Ni containing catalysts optimization of the preparation conditions e.g. urea concentration is required. Excess urea is required initially since solutions of Ce and Zr salts are highly acidic ($\text{pH} < 2$). On the other hand, low urea concentration is needed to prevent formation of stable ammonium Co and Ni complexes.

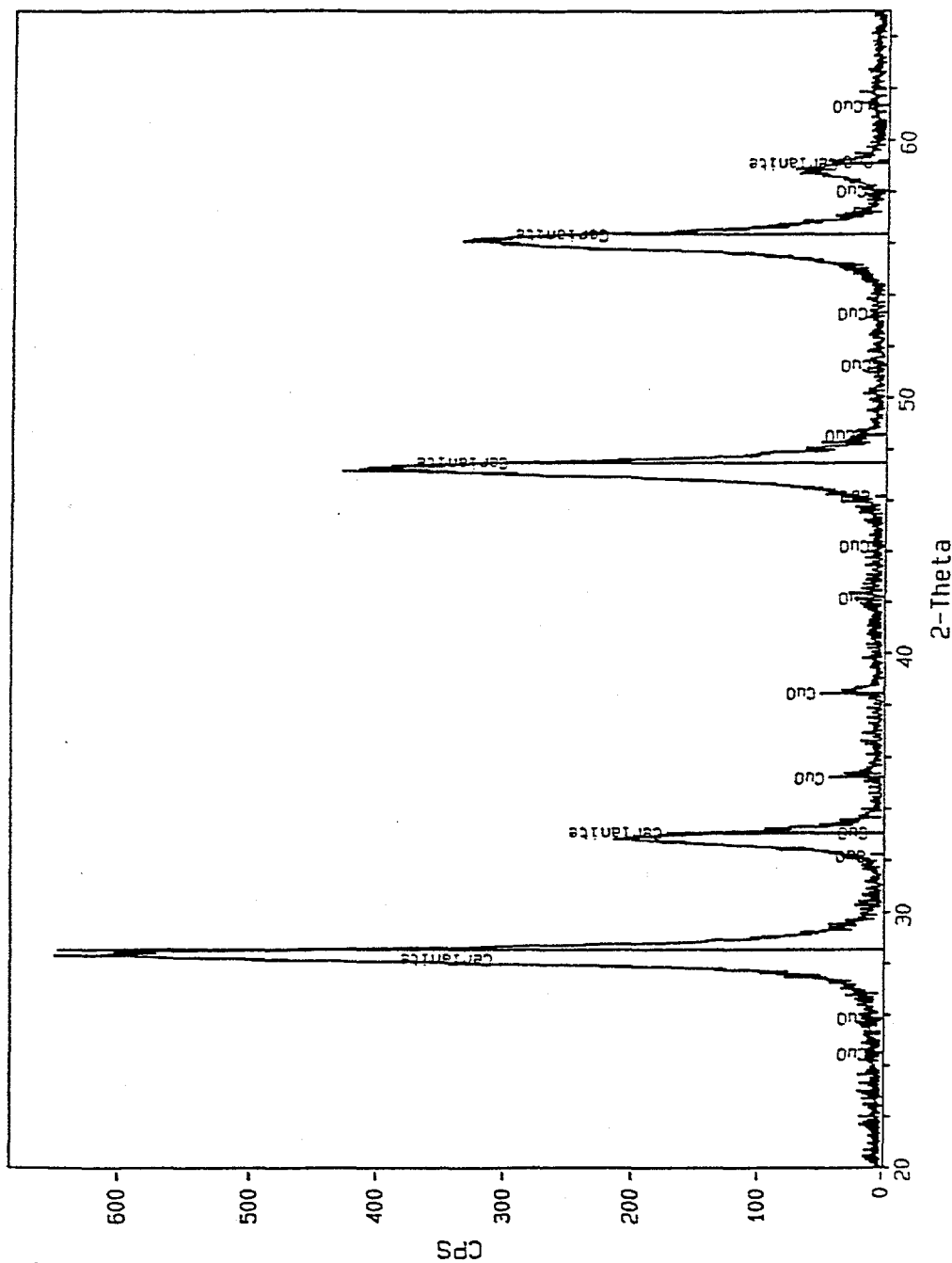
Total BET surface area was routinely measured by single-point N_2 adsorption and desorption on a Micromeritics PulseChemiSorb 2705 instrument. The catalyst sample in the single point measurement was pretreated by 30 minutes heating in helium flow at 200°C. Each measurement was typically of about 30 minutes duration. The BET surface areas of the prepared catalysts are listed in Table 4-2. Surface area was strongly affected by calcination temperature and by the type of doping element. 15% Cu-Ce (D) catalysts had surface areas of 30-40 m^2/g with exception of Sr- and Ca- doped catalysts which had 66 m^2/g and 4 m^2/g , respectively. Similar behavior was observed for Co and Ni containing catalysts. Zr-based catalysts had generally higher BET surface area than the corresponding Ce-based catalysts. Higher BET surface area was generally obtained at lower transition metal concentration (e.g. 5% Cu-Ce (La) and 5% Co-Ce (La) had BET surface area about 60 m^2/g), but the surface area generally decreased to 10-20 m^2/g after heating to 750°C.

Table 4-2: Total BET Surface Area of Various Mixed Oxide Catalysts

Catalyst	Calcination temperature (°C)	Surface area (m ² /g)	Catalyst	Calcination temperature (°C)	Surface area (m ² /g)
15%Cu-Ce(La)	700	32.3	15%Cu-Zr(Y)	650	44.1
15%Cu-Ce(Gd)	650	40.2	15%Cu-Zr(La)	650	71.8
15%Cu-Ce(Y)	650	36.3	5%Cu-Zr(Y)	500	94.6
15%Cu-Ce(Mg)	650	34.4	Zr(Y)O ₂	500	101.2
15%Cu-Ce(Ca)	650	4.1	15%Co-Zr(Y)	650	31.8
15%Cu-Ce(Sr)	650	66	5%Co-Zr(Y)	500	92.1
20%Cu-Ce(La)	650	49.2	15%Co-Ce(La)	500(650)	154.4(63.2)
10%Cu-Ce(La)	650	29.6	15%Co-Ce(La)	700	17.3
5%Cu-Ce(La)	650	108.9	5%Co-Ce(La)	650	74.6
3%Cu-Ce(La)	650	119.9	15%Ni-Ce(La)	650	60.4

X-ray powder diffraction analysis of catalyst samples was performed on a Rigaku 300 X-ray Diffractometer with Rotating Anode Generators and monochromatic detector. Sample preparation consisted of grinding the catalyst powder as fine as possible, well mixing the powder with a resin solution, pouring the solution on a glass stub, and drying the sample in an oven at 90°C for 30 min. Copper K α 1 radiation was used with power setting at 60 kV and 300 mA. For crystal phase identification, typical operation parameters were divergence slit of 1°, scattering slit 1°, receiving slit 0.3°, and a scan rate 5°/min with 0.02 data interval.

XRD patterns for several Ce- and Zr-based catalysts are shown in Figure 4-1 through Figure 4-6, respectively. Major phases identified were CeO₂ and ZrO₂. Only in the case of 15%Cu-Ce(La) catalyst small CuO peaks were observed, whereas the 15%Cu-Zr(Y) catalyst showed only peaks corresponding to ZrO₂. Similarly, the XRD pattern of Co and Ni containing catalysts shows the presence of CeO₂ and ZrO₂ phases only, indicating that Co and Ni oxides are present as very small particles or clusters which can not be detected by XRD.



1> 44-0706: CuO - Copper Oxide
 2> 43-1002: Cerianite, syn - CeO2

case @ MIT - Fri Jan 12 1996 02:08pm

Figure 4-1: XRD Pattern of 15%Cu-Ce(La)-O

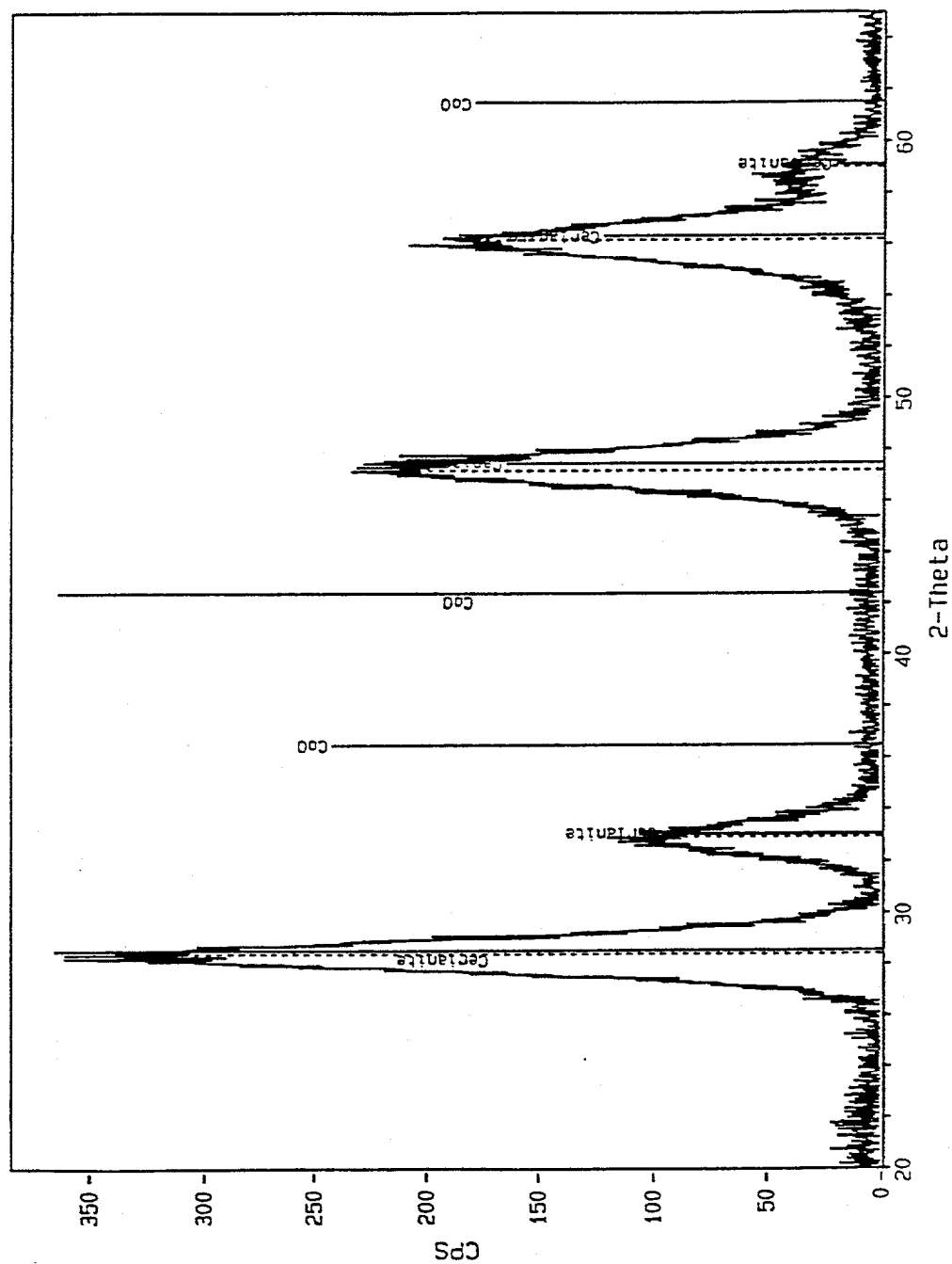
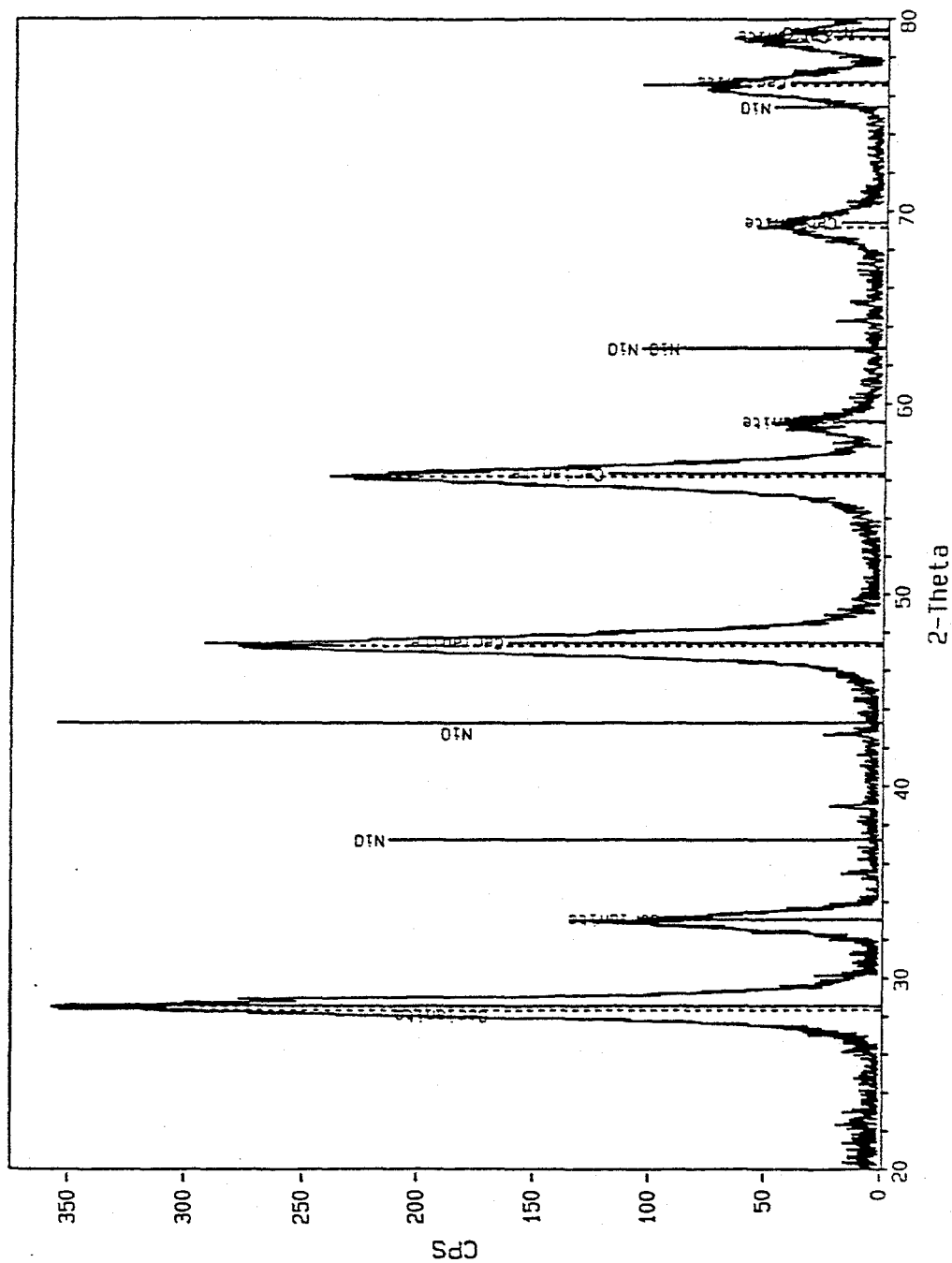


Figure 4-2: XRD Pattern of 15%Co-Ce(La)-O

ID: 15%NI CE (LA) - 9/5/95, 12-JAN-96@13:35
 File: Z00925.RAW Scan: 20-80/.02/ 10/#3001, Anode: CU



1> 43-1002: Cerianite, syn - CeO2 2> 44-1159: NiO - Nickel Oxide

cmse @ MIT - Fri Jan 12 1996 @2:56pm

Figure 4-3: XRD Pattern of 15%Ni-Ce(La)-O

File: Z00417.RAW Scan: 20-80/.02/ 2/#3001, Anode: CU

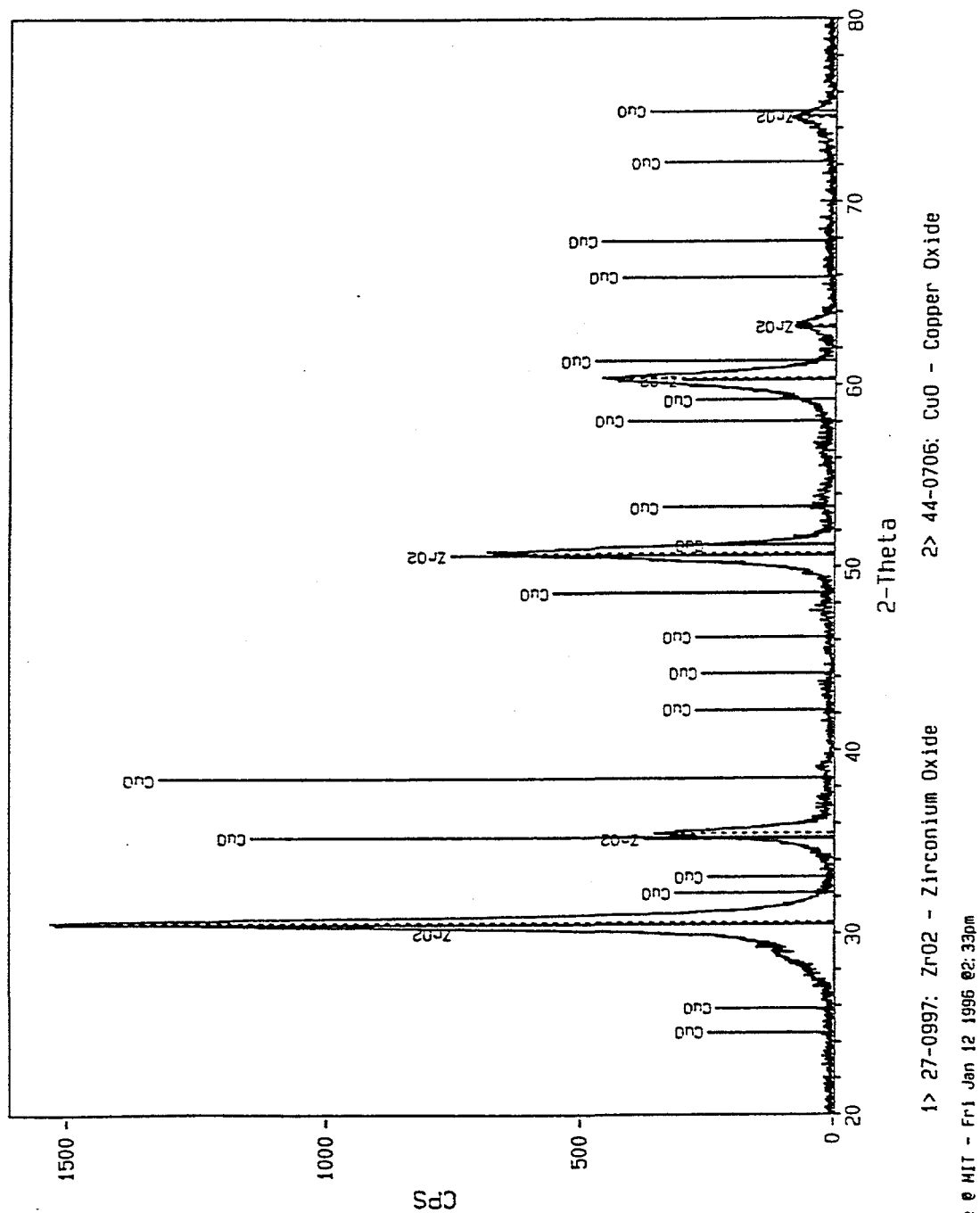
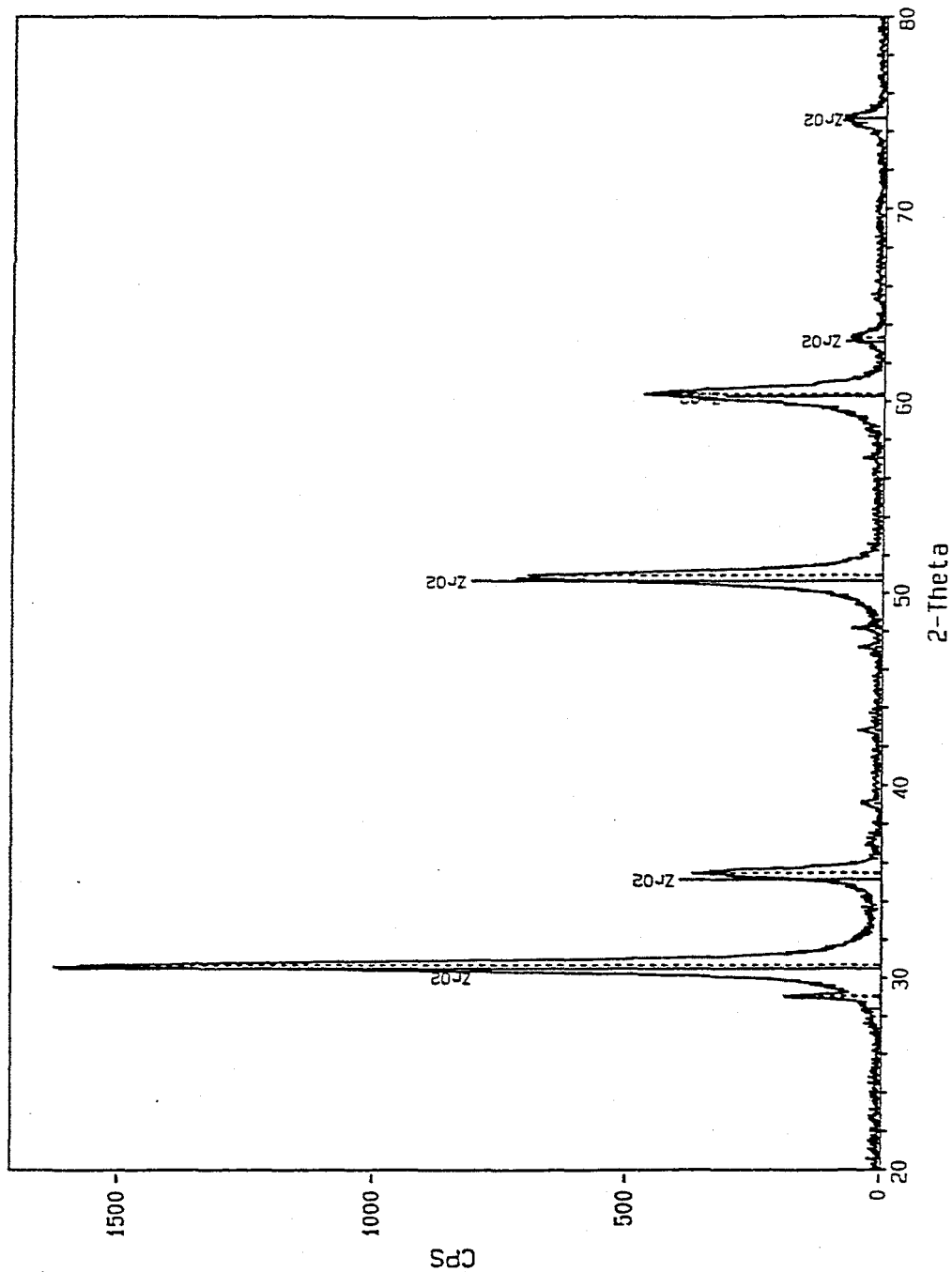


Figure 4-4: XRD Pattern of 15%Cu-Zr(Y)-O



1> 27-0997: ZrO2 - Zirconium Oxide

cmse @ MIT - Fri Jan 12 1996 @2:47pm

Figure 4-5: XRD Pattern of 15%Co-Zr(V)-O



Figure 4-6: XRD Pattern of 15%Ni-Zr(Y)-O

5. Plans for Next Quarter

5.1 Catalyst Development Work

Further analysis of these catalysts by XRD is planned for next quarter. Also, elemental analysis of the catalysts by Inductively Coupled Plasma emission spectroscopy (ICP) is planned. Screening microreactor tests will begin, using $\text{CH}_4/\text{SO}_2/\text{He}$ gas mixtures. Parallel studies of the reducibility of these oxide composite catalysts will be conducted by temperature-programmed reduction.

5.2 Process Evaluation Work

Next quarter we plan to initiate the market process and cost evaluation work. We will identify the regenerable sorbent technologies that could benefit from advanced byproduct recovery. We will establish the key technical and economic criteria that must be met by the catalytic SO_2 reduction process.

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 Ellision, 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.
4. Flytzani-Stephanopoulos, M. et al., "Selective Catalytic Reduction of Sulfur Dioxide to Elemental Sulfur", Final Report to DOE, Grant No. DE-FG-22-92PC92534 (1995).
5. Liu, W., Sc.D. Thesis, MIT, May 1995.
6. Liu, W., Sarofim, A.F., Flytzani-Stephanopoulos, M., *Appl. Catal. B*, (1994) 4, 167-186.
7. Flytzani-Stephanopoulos, M., Liu, W., Composite Catalyst for Carbon Monoxide and Hydrocarbon Oxidation, U.S. Patent Application. (allowed, Sept. 1995).
8. Liu, W., Sarofim, A.F., Flytzani-Stephanopoulos, M., (1994) *Chem.Eng.Sci.*, 49 (24A), 4871-4888.
9. Liu, W. and Flytzani-Stephanopoulos, M., (1995) *J. Catal.*, 153, 304.
10. Liu, W. and Flytzani-Stephanopoulos, M., (1995) *J. Catal.*, 153, 317.
11. Liu, W., Flytzani-Stephanopoulos, M., U.S. Patent No. 5, 384, 01 (1995).
12. Aiken, B., Hsu, W.P., Matijevic, C., (1988) *J. Am. Ceram. Soc.*, 71 (10), 845-853.