**DOE/PC/81004-T3
(DE92008465)**

**FLUIDIZED-BED COPPER OXIDE PROCESS
Proof-of-Concept Unit Design**

**By
P. P. Shah
G. S. Takahashi
D. G. Leshock**

October 14, 1991

Work Performed Under Contract No. AC22-85PC81004

**For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania**

**By
UOP, Inc.
Des Plaines, Illinois**

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.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

DOE/PC/81004--T3

DE92 008465

FLUIDIZED-BED COPPER OXIDE PROCESS

Proof-of-Concept Unit Design

Prepared for the
United States Department of Energy
Under Contract No. DE-AC22-85PC 81004

by

P. P. Shah, G. S. Takahashi, and D. G. Leshock

UOP
Des Plaines, Illinois

October 14, 1991

ABSTRACT

The fluidized-bed copper oxide process was developed to simultaneously remove sulfur dioxide and nitrogen oxide contaminants from the flue gas of coal-fired utility boilers. This dry and regenerable process uses a copper oxide sorbent in a fluidized-bed reactor. Contaminants are removed without generating waste material.

The Pittsburgh Energy Technology Center (PETC) of the U.S. Department of Energy had demonstrated the technical potential of the fluidized-bed copper oxide process through several stages of bench-scale and pilot plant testing. UOP continued this effort in a testing program with a 100 SCFM life-cycle test unit (LCTU). The LCTU program was completed in March 1987. During this testing, UOP demonstrated that the process is capable of simultaneously removing up to 90 vol-% of the sulfur dioxide and nitrogen oxide contaminants from coal-derived flue gas over extended periods.

UOP completed the design of a 2,500 SCFM proof-of-concept unit based on results of the LCTU testing. In addition, UOP's experience with CCR* continuous regeneration systems and its expertise in the production of attrition-resistant catalyst base, catalyst fluidization as applied in fluid catalytic cracking (FCC), and copper oxide adsorption and regeneration chemistry were directly applied to the design of the 2,500 SCFM proof-of-concept unit.

This report summarizes the work done under Phase II of the program: "Design of the 2,500 SCFM Proof-of-Concept Unit."

CONTENTS

Abstract	iii
Tables	x
Figures	x
1.0 Introduction and Background	1.1
1.1 Process Development Background	1.3
1.2 Process Chemistry and Configuration	1.4
2.0 Life-Cycle Test Unit Results	2.1
2.1 LCTU Operations Summary	2.1
2.2 Variable Study	2.7
2.3 Sorbent Attrition	2.17
2.4 LCTU Program Conclusions	2.17
3.0 Proof-of-Concept Unit Design	3.1
3.1 Design Objectives	3.2
3.2 Scope of Design	3.2
4.0 Proof-of-Concept Unit Design Basis	4.1
4.1 Kincaid Station Operating Conditions	4.1
4.2 2,500 SCFM Unit Design Basis	4.1
4.2.1 Feedstock (Flue Gas)	4.2
4.2.2 Product(s)	4.2
4.2.3 Process Conditions	4.2
5.0 Process Description	5.1
5.1 Flue Gas Routing	5.1
5.1.1 Supply	5.1
5.1.2 Flue Gas Heating	5.1
5.1.3 NH ₃ Injection	5.3

5.1.4	Absorber	5.3
5.1.5	Treated Flue Gas	5.3
5.2	Circulating Gas	5.4
5.2.1	Circulating Gas Cooling	5.4
5.2.2	Circulating Gas Boosting	5.4
5.2.3	Circulating Gas Dust Collection	5.4
5.2.4	Circulating Gas Reheating	5.4
5.3	Lift Gas	5.4
5.3.1	Lift Gas Boosting	5.4
5.3.2	Lift Gas Flow Control	5.5
5.4	Natural Gas Heat-up for Regeneration	5.5
5.5	Regenerator Offgas Return	5.5
5.6	Sorbent Circulation	5.5
5.6.1	Fluidized Bed	5.5
5.6.2	Sorbent Heat-up	5.6
5.6.3	Absorber Buffer	5.6
5.6.4	Sorbent Regeneration	5.6
5.6.5	Sorbent Addition	5.6
5.6.6	Lock Hopper	5.7
5.6.7	Sorbent Lift	5.7
5.7	Nitrogen Flows	5.7
5.7.1	Regenerator	5.7
5.7.2	Absorber	5.7
5.7.3	Safety Shutdown	5.8
5.8	Circulating Cooling Air for Temperature Control	5.8
6.0	Component Design Basis	6.1
6.1	Absorber	6.1
6.1.1	Design Conditions	6.1
6.1.2	Fluidized Bed	6.2
6.1.3	Fluidized-Bed Grid	6.3
6.1.4	Flue Gas Plenum	6.3
6.1.5	Sorbent Heat-up Zone	6.4
6.1.6	Annular Distributor	6.4

6.1.7	Buffer Zone	6.4
6.1.8	Buffer Purge Zone	6.4
6.2	Regenerator	6.5
6.2.1	Design Conditions	6.5
6.2.2	Sorbent Inlet Pipe	6.5
6.2.3	Sorbent Bed	6.5
6.2.4	Annular Distributor	6.5
6.2.5	Sorbent Outlet	6.5
6.3	Solids Transfer System	6.6
6.3.1	Lock Hopper	6.6
6.3.1.1	Design Conditions	6.6
6.3.1.2	Sizing	6.6
6.3.1.3	Cycle Time	6.6
6.3.2	Lift Engager	6.7
6.3.2.1	Design Conditions	6.7
6.3.2.2	Lift Pipes	6.7
6.3.2.3	Sizing of the Lift Engager	6.7
6.4	General Design Requirements for the Flue Gas Heater	6.7
6.5	Circulating Gas Circuit	6.8
6.5.1	Circulating Gas Exchanger	6.8
6.5.2	Circulating Gas Cooler	6.8
6.5.3	Circulating Gas Dust Collector	6.8
6.6	General Design Requirements of the Regeneration Gas Heater	6.8
6.7	Insulation	6.9
7.0	Plant Layout and Configuration	7.1
7.1	Stacked versus Side-by-side	7.1
7.2	Absorber versus Regenerator on Top	7.1
7.3	General Layout	7.2
8.0	Instrumentation and Control	8.1
8.1	General Instrumentation	8.1

8.1.1	Digital Controllers	8.1
8.1.2	Analog Controllers	8.1
8.1.3	Critical Alarms and Shutdowns	8.1
8.2	Programmable Logic Controller	8.2
8.3	Analyzers	8.2
8.3.1	SO ₂ and NO _x	8.2
8.3.2	Oxygen	8.2
8.3.3	Methane	8.2
9.0	Safety	9.1
9.1	General	9.1
9.1.1	Safety Equipment Specification	9.1
9.1.2	Material Safety Data	9.1
9.2	Atmosphere Isolation with Buffers	9.1
9.2.1	Absorber Buffer	9.1
9.2.2	Regenerator Buffer	9.2
9.3	Shutdown Systems	9.2
9.3.1	Host-Unit Main Shutdown Switch	9.2
9.3.2	Emergency Board and Field Shutdown Switches	9.2
9.3.3	Flue Gas Heater	9.2
9.3.4	Upper Isolation System	9.3
9.3.5	Lower Isolation System	9.3
9.3.6	Regeneration Gas and Ammonia Injection	9.3
9.4	Relief Valves	9.4
10.0	Test Strategy	10.1
10.1	Test Plan Development	10.1
10.2	Unit Shakedown	10.1
10.3	Key Process Variables	10.2
10.3.1	Sorbent Bed Heights	10.2
10.3.2	Cu/S Mole Ratio	10.3
10.3.3	Absorber Temperature	10.3
10.3.4	NH ₃ /NO _x Ratio	10.4

10.3.5	Regenerator Temperature and Time	10.4
10.3.6	Flue Gas Constituents	10.4
10.4	Process Variable Study	10.4
10.4.1	Variables	10.5
10.4.2	Regenerator Experimental Plan	10.6
10.4.3	Absorber Experimental Plan	10.6
10.4.4	Other Absorber Experiments	10.8
10.5	Schedule	10.8
10.6	Reliability Test	10.9
10.7	Facility Dismantling	10.10
11.0	Unit Operating Procedures	11.1
11.1	Unit Description	11.1
11.1.1	Absorber	11.1
11.1.2	Regenerator	11.1
11.1.3	Sorbent Transfer System	11.2
11.2	Unit Precommissioning and Start-up	11.2
11.2.1	Unit Checkout	11.2
11.2.2	Sorbent Attrition	11.2
11.2.3	Warm-Up and Circulation	11.3
11.2.4	Flue Gas to Absorber	11.3
11.3	Unit Shutdown	11.4
11.3.1	Routine Shutdown	11.4
11.3.2	Emergency Shutdown	11.5
References		R.1

TABLES

1.1	Coal Properties Reported on "As-Received Basis"	1.3
2.1	LCTU Testing Summary	2.2
4.1	Feedstock Composition	4.1
4.2	Absorber Process Conditions	4.3
4.3	Regenerator Process Conditions	4.3
8.1	Analytical Instrumentation for Gas Analysis	8.3
10.1	Experimental Conditions	10.7

FIGURES

1.1	Life-Cycle Test Facility.....	1.2
1.2	Schematic Flue Gas Flow Diagram of Boiler System with Flue Gas Treating	1.6
2.1	Extended Performance of SOX-3 (Test 1)	2.8
2.2	Extended Performance of SOX-3 (Test 2)	2.9
2.3	Sorbent Circulation Effect	2.11
2.4	Sorbent Circulation and Bed Height Effect	2.12
2.5	Absorber Temperature Effect	2.13
2.6	Sorbent Circulation Effect for SOX-3 and SOX-4	2.14
2.7	Bed Height Effect	2.15
2.8	Absorber Temperature Effect for SOX-3 and SOX-4	2.16
5.1	Process Flow Diagram of 2,500 SCFM Fluidized-Bed Copper Oxide Process	5.2

1.0 INTRODUCTION AND BACKGROUND

UOP began work on a research program designed to demonstrate the technical and economic feasibility of the fluidized-bed copper oxide process in 1985 with the Pittsburgh Energy Technology Center (PETC) of the U.S. Department of Energy (DOE). The program consisted of the following four phases:

- Sorbent testing in a 100 SCFM life-cycle test unit (LCTU)
- Design and construction of a 2,500 SCFM proof-of-concept unit
- Operation of the 2,500 SCFM proof-of-concept unit
- Conceptual design and economic evaluation of a 500 MW commercial unit

Sorbent testing in the 100 SCFM LCTU was completed in March 1987. The results from this testing are reported in Section 2.0 of the report.

The LCTU was designed and built under PETC supervision and operated by UOP personnel in Pittsburgh during a six-month testing period. Figure 1.1 shows a simplified process flow diagram of this unit. In the process flow, sorbent was continuously transferred between the absorber and regenerator vessels to allow for continuous and integrated operation.

The transfer of spent sorbent between the absorber and regenerator was accomplished with a transfer hopper system using nitrogen as the lift gas. Methane was used to regenerate the sorbent in the moving-bed regenerator. Sorbent flow was by gravity from the stacked regenerator to the absorber through a lock hopper system. Contaminant removal was accomplished in the fluidized-bed reactor.

Flue gas for the LCTU was generated in a 40 lb/h coal combustor adjacent to the unit. Lower Kittanning coal, described in Table 1.1, was used during all testing reported in Section 2.0. Anhydrous sulfur dioxide (SO_2) was injected into the furnace as required to control the SO_2 concentration in the flue gas.

FIGURE 1.1
PROCESS FLOW DIAGRAM
OF LIFE-CYCLE TEST FACILITY

UOP 1571-7
UOP 1847-1

Table 1.1
Coal Properties
Reported on an As-Received Basis

<u>LCTU Testing</u>	<u>Lower Kittanning Seam</u>
Heating Value, Btu/lb	12,897
Sulfur, wt-%	2.80
Ash, wt-%	5.95
Moisture, wt-%	5.52

<u>Kincaid Station</u>	<u>Illinois Peabody Mine No. 10</u>
Heating Value, btu/lb	10,300
Sulfur, wt-%	3.40
Ash, wt-%	9.70
Moisture, wt-%	17.60

Information obtained during the life-cycle testing program was used to design the 2,500 SCFM proof-of-concept unit for operation at Commonwealth Edison's Kincaid, Illinois, station. This unit was designed to simultaneously remove 90 vol-% of the SO₂ and NO_x contaminants from a flue gas slipstream. Illinois Peabody Coal No. 10, described in Table 1.1, is used at the Kincaid station.

The proof-of-concept unit design and construction was sponsored by the PETC and the State of Illinois Department of Energy and Natural Resources.

1.1 PROCESS DEVELOPMENT BACKGROUND

In 1970, McCrea showed that copper oxide sorbent absorbed SO₂ in a fixed-bed reactor.¹ Bench-scale testing during this period demonstrated that the sulfated sorbent could be regenerated with hydrogen or methane to produce a concentrated stream of SO₂.

In 1976, UOP demonstrated that copper oxide (CuO) sorbent is capable of absorbing SO₂ from the flue gas of coal-fired utility boilers.² This testing was completed in a 0.5 MW pilot plant

using a fixed-bed reactor and processing the flue gas of a commercial coal-fired utility boiler. The ability to simultaneously absorb SO_2 on the sorbent while selectively reducing NO_x with ammonia (NH_3) was subsequently demonstrated by UOP in 1980 in the 0.5 MW pilot plant.³

The use of the CuO sorbent to treat flue gas in a fluidized-bed reactor rather than a fixed-bed reactor was reported by Strakey in 1979.⁴ In this test, a 6-inch diameter fluidized-bed reactor was used to treat the combustion products of natural gas.

Data obtained in the Strakey study were used by PETC to design a 40- by 48-inch fluidized-bed reactor that processed flue gas generated from a 500 lb/h coal-combustion facility. The results of this testing, which were reported by Yeh in 1984, demonstrated that 90 vol-% removal of SO_2 and NO_x can be achieved in a fluidized-bed reactor processing the combustion products of high-sulfur coal.⁵ The regeneration of the sulfated sorbent was accomplished using a batch-type operation rather than a continuous mode.

Using the data from these testing programs, a preliminary economic analysis of the process was completed in 1983.⁶ The design configuration used was for a 500 MW unit capable of removing 90 vol-% of the SO_2 and NO_x contaminants in the flue gas of the coal-fired utility boilers. This analysis indicated that the process compared favorably with both conventional wet-scrubbing flue gas treating systems and other, more advanced, regenerable processes.

1.2 PROCESS CHEMISTRY AND CONFIGURATION

The fluidized-bed copper oxide process links the chemical absorption of SO_2 on CuO sorbent with the selective reduction of NO_x in the presence of NH_3 . Copper sulfate (CuSO_4), formed by the absorption of SO_2 , acts as a catalyst for the reduction of NO_x .

The process configuration consists of four primary sections:

- Absorber
- Regenerator
- Sorbent transfer system
- Sulfur recovery unit

These sections have been incorporated into the proposed design to provide efficient flue gas treating with continuous sorbent regeneration.

Flue gas contaminant removal is accomplished in a fluidized bed of CuO sorbent. The fluidized-bed configuration provides for intimate contact between the flue gas and sorbent and for efficient heat distribution in the reaction zone.

The following equation describes the absorption of SO₂ with CuO:

The absorption of SO₂ proceeds rapidly at temperatures of 700 to 800°F. The process is located in the hot section of the utility flue gas ducting upstream of the air preheater. This configuration is illustrated in Figure 1.2. Hot operation has a significant advantage because the need to reheat the flue gas after treating is eliminated. Plugging and scaling of process equipment is also reduced.

The reduction of NO_x with NH₃ in the presence of CuSO₄ is described by the following equations:

Overall, the reactions proceeding in the fluidized bed are exothermic. Higher temperatures at the outlet of the absorber and additional heat recovery in the air preheater will result. Fly ash passes through the fluidized bed with negligible effect on sorbent reactivity and with minimal scaling or plugging problems.

The fluidized-bed process almost completely removes sulfur trioxide (SO₃) from the flue gas according to the following equation:

FIGURE 1.2
SCHEMATIC FLUE GAS FLOW DIAGRAM
OF BOILER SYSTEM WITH FLUE GAS TREATING

LEGEND

- FGT - FLUE GAS TREATING
- ESP - ELECTROSTATIC PRECIPITATOR
- ID - INDUCED DRAFT
- FD - FORCED DRAFT

The elimination of this contaminant from the flue gas reduces problems caused by acid precipitation in cooler downstream equipments and allows the utility to recover additional heat without increased corrosion. The additional heat is acquired by lowering stack temperatures.

Spent sorbent is continuously withdrawn from the absorber and transferred pneumatically to a gravity-flow regenerator. Hydrogen, carbon monoxide, or methane can be used to regenerate the spent sorbent. The regeneration of the sorbent with methane is described by the following equation:

Copper formed during the regeneration step is immediately oxidized with oxygen in the flue gas according to the following equation:

The regeneration of the sorbent material produces a stream of concentrated SO_2 that can be converted to salable elemental sulfur or sulfuric acid using commercially available sulfur-recovery processes. In this manner, the need for costly disposal of waste is eliminated.

2.0 LIFE-CYCLE TEST UNIT RESULTS

The objectives of the testing program completed in March 1987 by UOP in the 100 SCFM life-cycle test unit were to:

- Demonstrate the simultaneous removal of 90 vol-% of the SO_2 and NO_x contaminants from coal-derived flue gas
- Observe the performance of the CuO sorbent during extended operations over multiple cycles of absorption and regeneration
- Determine the effects of varying process operating conditions on contaminant removal efficiency

All of these objectives were accomplished during the testing program. Complete details of the testing program have been published.^{8,9,10}

2.1 LCTU OPERATIONS SUMMARY

Two UOP sorbent materials were tested. Both sorbents were prepared on alumina-based spheres impregnated to a nominal 7.0 wt-% copper concentration. However, other properties of these sorbents were quite different. As will be shown later in Section 2.2, these differences led to significantly different sorbent performance.

Table 2.1 summarizes the operating conditions and results of the tests (Nos. 1-25) completed in the life-cycle testing program. The copper-to-sulfide mole ratios (Cu/S) reported in this table show the level of copper utilization required to achieve the reported level of SO_2 removal at each set of operating conditions. This ratio is dependent on the flow rate and SO_2 concentration of the flue gas as well as the circulation rate and copper concentration of the sorbent. The calculation of the Cu/S mole ratio assumes that the sorbent is completely regenerated when entering the absorber and, accordingly, all the copper on the sorbent is available for SO_2 removal.

In a related fashion, the NH_3/NO_x mole ratios for each test are reported in Table 2.1 to indicate the level of NH_3 utilization during NO_x removal at each set of operating conditions.

Table 2.1
LCTU Testing Summary

	<u>Test No.</u>				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Sorbent	SOX-3	SOX-3	SOX-3	SOX-3	SOX-3
Cumulative Cycle No.	331	399	447	510	539
Flue Gas Flow Rate, SCFM	104	105	104	97	99
Sorbent Circulation, lb/min	4.1	4.1	4.0	4.1	2.1
lb/Sorbent/1,000 SCF Flue Gas	39.2	39.2	39.6	42.9	21.2
Absorber Temp, °F	796	802	746	696	694
Residence Time, min	18	18	18	18	34
Regenerator Temp, °F	848	858	829	806	851
Residence Time, min	37	42	46	46	75
Cu/S Mole Ratio	6.0	5.9	6.1	6.6	3.3
NH ₃ /NO _x Mole Ratio	0.8	1.3	0.8	1.0	1.1
Bed Height, in.	36	36	36	36	36
Sorbent Inventory, lbs:					
System	280	328	344	345	314
Regenerator	122	170	186	187	156
SO ₂ Absorber Inlet, ppmv	2,495	2,430	2,426	2,418	2,423
% SO ₂ Removal	88.8	89.7	88.4	88.7	84.2
NO _x Absorber Inlet, ppmv	381	426	491	448	455
% NO _x Removal	77.0	90.6	92.3	91.3	91.3
Attrition in the Test					
Period, wt-%	0.22	0.12	0.12	0.15	--
Pressure Drop, in. H ₂ O	15.9	14.6	15.2	15.3	13.3

(continued)

Table 2.1 (continued)
LCTU Testing Summary

	<u>Test No.</u>				
	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Sorbent	SOX-3	SOX-3	SOX-3	SOX-3	SOX-3
Cumulative Cycle No.	566	570	588	604	627
Flue Gas Flow Rate, SCFM	100	105	103	103	78
Sorbent Circulation, lb/min	2.1	1.1	3.6	4.0	3.6
lb Sorbent/1,000 SCF Flue Gas	20.3	10.5	35.5	38.4	45.5
Absorber Temp, °F	802	800	799	797	711
Residence Time, min	34	62	19	19	21
Regenerator Temp, °F	867	944	850	839	828
Residence Time, min	75	170	47	47	53
Cu/S Mole Ratio	3.5	1.7	5.5	6.0	7.1
NH ₃ /NO _x Mole Ratio	1.3	1.1	0.7	0.7	1.1
Bed Height, in.	36	36	36	36	36
Sorbent Inventory, lbs:					
System	314	345	345	345	345
Regenerator	156	187	187	187	187
SO ₂ Absorber Inlet, ppmv	2,375	2,342	2,442	2,430	2,439
% SO ₂ Removal	85.9	77.4	94.4	89.4	90.0
NO _x Absorber Inlet, ppmv	436	420	421	474	123
% NO _x Removal	90.5	91.2	78.4	77.2	91.0
Attrition in the Test					
Period, wt-%	0.11	--	--	--	0.14
Pressure Drop, in. H ₂ O	12.9	12.0	24.5	14.8	14.1

(continued)

Table 2.1 (continued)
LCTU Testing Summary

	<u>Test No.</u>				
	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>
Sorbent	SOX-3	SOX-3	SOX-3	SOX-3	SOX-3
Cumulative Cycle No.	666	704	723	741	763
Flue Gas Flow Rate, SCFM	103	103	104	100	102
Sorbent Circulation, lb/min	4.0	4.0	4.1	4.0	2.0
lb/Sorbent/1,000 SCF					
Flue Gas	39.6	37.9	39.4	40.0	20.1
Absorber Temp, °F	800	802	799	698	697
Residence Time, min	7	7	7	7	10
Regenerator Temp, °F	860	859	858	814	846
Residence Time, m	46	46	46	45	90
Cu/S Mole Ratio	6.3	6.1	5.3	6.2	3.1
NH ₃ /NO _x Mole Ratio	1.5	3.5	0.8	2.3	3.2
Bed Height, in.	18	18	18	18	18
Sorbent Inventory, lbs:					
System	302	302	301	301	301
Regenerator	187	187	186	186	186
SO ₂ Absorber Inlet, ppmv	2,365	2,425	2,384	2,476	2,436
% SO ₂ Removal	79.8	84.1	84.9	78.9	68.7
NO _x Absorber Inlet, ppmv	287	421	402	364	386
% NO _x Removal	77.7	90.5	77.1	89.8	89.8
Attrition in the Test					
Period, wt-%	--	0.14	--	--	--
Pressure Drop, in. H ₂ O	6.1	6.0	6.0	5.9	6.0

(continued)

Table 2.1 (continued)
LCTU Testing Summary

	<u>Test No.</u>				
	<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>
Sorbent	SOX-3	SOX-3	SOX-3	SOX-3	SOX-4
Cumulative Cycle No.	779	798	833	850	54
Flue Gas Flow Rate, SCFM	102	102	102	101	104
Sorbent Circulation, lb/min	2.1	3.9	4.0	4.0	4.0
lb Sorbent/1,000 SCF Flue Gas	21.8	38.2	40.2	39.4	38.4
Absorber Temp, °F	802	793	803	801	800
Residence Time, min	10	19	18	19	--
Regenerator Temp, °F	889	833	827	827	871
Residence Time, min	89	44	43	43	63
Cu/S Mole Ratio	3.1	6.1	6.6	6.6	5.9
NH ₃ /NO _x Mole Ratio	3.2	0	1.3	0.7	0.9
Bed Height, in.	18	36	36	36	18
Sorbent Inventory, lbs:					
System	301	330	330	330	393
Regenerator	186	172	172	172	250
SO ₂ Absorber Inlet, ppmv	2,486	2,383	2,315	2,269	2,492
% SO ₂ Removal	68.5	88.7	87.6	87.4	70.7
NO _x Absorber Inlet, ppmv	383	476	484	490	410
% NO _x Removal	89.8	0.0	90.8	69.6	89.7
Attrition in the Test					
Period, wt-%	--	--	--	0.13	0.18
Pressure Drop, in. H ₂ O	5.7	16.2	16.1	15.9	9.9

(continued)

Table 2.1 (continued)
LCTU Testing Summary

	<u>Test No.</u>				
	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u>	<u>25</u>
Sorbent	SOX-4	SOX-4	SOX-4	SOX-4	SOX-4
Cumulative Cycle No.	97	122	175	195	275
Flue Gas Flow Rate, SCFM	101	102	102	102	101
Sorbent Circulation, lb/min	4.1	2.0	4.0	2.0	4.0
lb Sorbent/1,000 SCF					
Flue Gas	39.5	19.8	37.3	19.9	39.4
Absorber Temp, °F	703	799	798	801	800
Residence Time, min	--	--	--	--	--
Regenerator Temp, °F	812	843	841	861	846
Residence Time, min	60	125	63	129	62
Cu/S Mole Ratio	6.3	3.1	6.1	3.0	6.2
NH ₃ /NO _x Mole Ratio	0.9	0.8	1.0	0.9	1.3
Bed Height, in.	18	18	36	36	36
Sorbent Inventory lbs:					
System	390	390	455	455	455
Regenerator	247	247	249	249	249
SO ₂ Absorber Inlet, ppmv	2,542	2,449	2,440	2,429	2,425
% SO ₂ Removal	66.6	65.6	82.4	79.0	85.7
NO _x Absorber Inlet, ppmv	435	392	363	368	450
% NO _x Removal	90.5	89.9	90.6	90.1	91.8
Attrition in the Test					
Period, wt-%	0.21	0.23	0.18	0.09	0.12
Pressure Drop, in. H ₂ O	10.0	9.0	20.3	18.4	19.8

The first UOP sorbent, designated SOX-3, was shown to remove approximately 90 vol-% of the SO_2 contaminant from flue gas at an absorber temperature of 800°F and a 6.0 Cu/S mole ratio. Approximately 77 vol-% of the NO_x was simultaneously removed at the reported 0.8 NH_3/NO_x mole ratio. Figure 2.1 shows the SOX-3 performance at these operating conditions over a continuous 96-hour period. During this time, the sorbent was subjected to approximately 60 cycles of absorption and regeneration.

The NH_3/NO_x mole ratio was next increased from 0.8 to 1.3 to achieve a 90 vol-% NO_x removal level. Except for the NH_3 injection rate, all other operating conditions were held constant. Figure 2.2 shows that approximately 90 vol-% of the SO_2 and NO_x contaminants were simultaneously removed over a continuous 65-hour period at these operating conditions. During this time, the sorbent was subjected to approximately 40 cycles of absorption and regeneration.

The SOX-3 sorbent eventually completed a total of 850 cycles. No significant decrease in sorbent performance was observed during this time, as shown by comparing sorbent performance at identical sets of operating conditions with increasing time on-stream. For example, Test 1 (Cycle No. 331), Test 9 (Cycle No. 604), and Test 19 (Cycle No. 850) were all run at the same set of operating conditions and, as indicated in Table 2.1, achieved consistent levels of contaminant removal. This performance indicated that the SOX-3 sorbent was not adversely affected by the fly ash and is capable of undergoing multiple cycles of absorption and regeneration without prohibitively high loss of reactivity.

The performance of SOX-3 at different sorbent circulation rates, absorber bed heights, and absorber temperatures was determined during the life-cycle testing program. This testing was undertaken to identify the interactions between process operating conditions and contaminant removal efficiency. Trade-offs between operating costs and contaminant removal efficiency were also determined.

The major operating costs associated with the fluidized-bed copper oxide process are expected to arise from sorbent attrition and power consumption. Operations with the LCTU have indicated that most of the sorbent attrition occurs in the lift lines during sorbent transfer and not in the fluidized-bed absorber. This result suggests that decreasing the sorbent circulation rate will lead

FIGURE 2.1
EXTENDED PERFORMANCE
OF SOX-3 (TEST 1)

UOP 1493-3
 UOP 1847-3

FIGURE 2.2
EXTENDED PERFORMANCE
OF SOX-3 (TEST 2)

to a corresponding and proportional decrease in sorbent attrition. The increase in absorber sorbent residence time associated with decreased sorbent circulation rates would not be expected to significantly affect the level of sorbent attrition.

Consequently, operating costs can be reduced by decreasing the sorbent circulation rate; however, as shown in Figure 2.3, this decrease will inevitably lead to lower levels of SO₂ removal. Figure 2.3 also shows that the removal of SO₂ decreases more rapidly at lower sorbent circulation rates. Even at the lowest circulation rate, however, the percentage of SO₂ removal remains quite high.

Increasing the absorber sorbent bed height increases the flue gas residence time in the sorbent bed and provides one means of maintaining the SO₂ removal level at lower sorbent circulation rates. However, higher bed heights lead to increased pressure drop through the absorber bed and an associated increase in operating costs through higher power consumption. Decreasing the absorber bed height leads to a corresponding and proportional decrease in absorber pressure drop and operating costs.

Figure 2.4 shows SO₂ removal levels over a range of sorbent circulation rates at two absorber bed heights and a constant 800°F absorber temperature. The SO₂ removal level decreased more rapidly at the lower sorbent bed height, and quite high sorbent circulation rates were required to maintain high levels of SO₂ removal at the lower absorber bed height.

Increasing the absorber temperature also increased the SO₂ removal level; however, as shown in Figure 2.5, SO₂ removal was not a strong function of absorber temperature. Figure 2.5 shows SO₂ removal over a range of absorber temperatures at two sorbent circulation rates and a constant 36-inch bed height. At both the higher and lower sorbent circulation rates, the effect of lowering the absorber temperature by 100°F did not significantly reduce the level of SO₂ removal. Quite high SO₂ removal levels were maintained even at the lower temperature and the lower sorbent circulation rate.

The second UOP sorbent, designated SOX-4, displayed significantly poor performance than SOX-3 at all sets of operating conditions. With SOX-4 sorbent, SO₂ removal was lower, and sorbent attrition levels were higher for different sorbent circulation rates (Figure 2.6), absorber bed heights (Figure 2.7) and absorber temperatures (Figure 2.8). The SOX-4 sorbent also had the

FIGURE 2.3
SORBENT CIRCULATION EFFECT

*TEST NUMBER (SEE TABLE 2.1)

UOP 1493-5
UOP 1847-5

FIGURE 2.4
SORBENT CIRCULATION AND
BED HEIGHT EFFECT

*TEST NUMBER (SEE TABLE 2.1)

UOP 1493-6
 UOP 1847-6

FIGURE 2.5
ABSORBER TEMPERATURE EFFECT

*TEST NUMBER (SEE TABLE 2.1)

UOP 1493-7
UOP 1847-7

FIGURE 2.6
SORBENT CIRCULATION EFFECT
FOR SOX-3 AND SOX-4

*TEST NUMBER (SEE TABLE 2.1)

UOP 1493-B
UOP 1847-B

FIGURE 2.7
BED HEIGHT EFFECT

***TEST NUMBER (SEE TABLE 2.1)**

UOP 1493-9
UOP 1847-9

FIGURE 2.8
ABSORBER TEMPERATURE EFFECT
FOR SOX-3 AND SOX-4

*TEST NUMBER (SEE TABLE 2.1)

UOP 1493-10
UOP 1847-10

disadvantage of higher absorber pressure drops at all sets of operating conditions. Because of the inferior performance of the SOX-4 sorbent, extensive testing of this material was not undertaken.

2.3 SORBENT ATTRITION

Sorbent attrition levels were carefully monitored throughout the life-cycle testing program. The attrition level is reported as the total weight of sorbent lost by attrition from the unit inventory during a specified period divided by the total weight of sorbent circulated during the same time. The weight of sorbent lost by attrition was determined by measuring differences in sorbent volume inventory.

The attrition of SOX-3 sorbent averaged approximately 0.13 wt-% of the catalyst circulation rate during the life-cycle testing program. This level of attrition remained constant throughout the testing period and did not vary significantly with different sets of operating conditions or with increasing sorbent life. The attrition of SOX-4 sorbent averaged approximately 0.18 wt-%. This higher attrition level was probably the result of the higher lift gas velocities needed to transfer the heavier SOX-4 sorbent.

2.4 LCTU PROGRAM CONCLUSIONS

Testing by UOP in a 100 SCFM life-cycle test unit demonstrated that the fluidized-bed copper oxide process is capable of simultaneously removing up to 90% of the SO₂ and NO_x contaminants from coal-derived flue gas during continuous operation over extended periods.

Sorbent attrition observed during this testing was higher than expected based on previous test programs; however, several design and operating modifications were identified that could reduce attrition to more acceptable levels. No significant reduction in sorbent performance was observed during the testing program. This result indicates that trace flue gas contaminants and fly ash do not significantly affect the sorbent during extended operating periods.

Operational and equipment modifications were identified that would reduce the sorbent attrition levels observed during LCTU testing. Most of these modifications dealt with the sorbent transport system that was designed for the LCTU. The modifications included provision of smooth surfaces in the transport lines, careful design of the joints and the valves, and elimination of sharp

edges in the transport lines. UOP's experience in designing commercial CCR systems was incorporated in the design of the sorbent transport system for the 2,500 SCFM proof-of-concept unit.

3.0 PROOF-OF-CONCEPT UNIT DESIGN

The design of the proof-of-concept unit for the fluidized-bed copper oxide process is the second phase of a four-phase project to develop a commercial flue gas treating process for the removal of SO_2 and NO_x from the flue gas of commercial power plant boilers burning coal that is high in sulfur. The first phase was the operation of a pilot plant or bench-scale life-cycle test unit (LCTU) to test sorbent activity and stability. The LCTU was designed and built under PETC supervision.

The proof-of-concept unit was designed to demonstrate the ability of the process to treat a slipstream of flue gas from an actual operating utility boiler. The design of the demonstration unit would replicate commercial operating parameters. However, the unit would be built with a higher degree of flexibility to determine optimum operating parameters.

The design of the proof-of-concept unit draws on technology and know-how developed by UOP in the area of fluidized beds employed in the UOP fluidized catalytic cracking (FCC) process, and the movement of solid catalysts employed in the CCR section of the UOP Platforming* process. This background technology, coupled with the results of the LCTU, helped form the basis of design for the proof-of-concept unit.

In general, the schematic flow of the unit evolved toward a more simplified process as various economic measures were weighed against the information to be gained in proving the concepts. Initial changes were directed at eliminating sections of the overall process that either did not need demonstration on a commercial scale or would not be practical for commercial power boilers. One change was the elimination of the option to use hydrogen as a regeneration gas. This change allowed the simplification of the unit equipment required to isolate hydrogen from flue gas.

The original capacity of the unit (10,000 SCFM) was based on the flue gas equivalent of a 5 MW power boiler. As an additional cost-cutting measure, the size of the unit was reduced to 25% of the 5 MW size. This reduction would enable capital and operating costs to be reduced without significant loss in the unit's ability to demonstrate the process.

3.1 DESIGN OBJECTIVES

The design had to meet the following objectives:

- Demonstrate 90% removal of SO_2 and NO_x from the flue gas.
- Demonstrate the activity and stability of the sorbent.
- Demonstrate the sorbent's resistance to attrition.
- Determine the optimum operating parameters to minimize capital and operating costs for a commercial size unit.
- Determine optimum NH_3/NO_x ratio without NH_3 breakthrough.

3.2 SCOPE OF DESIGN

UOP's scope of design for the proof-of-concept unit consists of the absorption section, where SO_2 is absorbed and NO_x is converted in a slipstream of flue gas from the host unit. The sorbent is continuously regenerated in the regeneration section and returned to the absorption section. The handling of the SO_2 concentrated regenerant stream for sulfur recovery is not within UOP's scope of study for this project. The regenerant offgas is thus remixed with the treated flue gas before it is returned to the host unit.

The scope of UOP's work consists of generating a basic engineering package specifying equipment to the extent necessary to ensure that the unit will perform as outlined in the design basis. The content of the design package includes the following:

- A flagged process flow diagram showing pressure, temperatures, and flow rates of all streams.
- Piping and instrument diagrams.
- Elevation and general arrangement drawings.
- Project specifications:
 - Basic engineering data
 - Fired heaters
 - Vessel shells and internals

- Heat exchangers
- Compressors and fans
- Instruments
- Electrical
- Piping
- Auxiliary equipment

This design package, along with standard UOP specifications, provides a contractor with sufficient information to fabricate the equipment and erect the unit. A copy of the above mentioned information has been delivered to PETC.

4.0 PROOF-OF-CONCEPT UNIT DESIGN BASIS

UOP completed the design of the 2,500 SCFM proof-of-concept unit based on the operating conditions at Commonwealth Edison's Kincaid Station and the results of the LCTU testing. In addition, UOP's experience with CCR continuous catalyst regeneration systems and its expertise in the production of attrition-resistant catalyst base and in catalyst fluidization (FCC) were directly applied to the design of the proof-of-concept unit.

4.1 KINCAID STATION OPERATING CONDITIONS

Commonwealth Edison's Kincaid Station is firing a 3.4 wt-% sulfur coal with a 9.7 wt-% ash content, and 17.6 wt-% moisture content. The take-off point for the flue gas slipstream to the proof-of-concept unit was chosen for convenience and not because it was physically where the fluidized bed would be expected to be located in a commercial application. Taking the flue gas from the discharge of the main boiler's temperature controlling gas-recirculation fans gave favorable hydraulic conditions and a more straightforward piping run to the proof-of-concept unit. The flue gas conditions to the proof-of-concept unit are a temperature range of about 640°F to 690°F and a fly ash loading of about 2 grains per dry SCF.

4.2 2,500 SCFM UNIT DESIGN BASIS

The design basis for the proof-of-concept is shown in Table 4.1.

Table 4.1
Feedstock Composition

<u>Component</u>	<u>Mol-%</u>
N ₂	73.38
O ₂	3.20
CO ₂	13.60
SO ₂	0.255
NO	0.062
NO ₂	0.003
H ₂ O	<u>9.50</u>
Total	100.0

4.2.1 Feedstock (Flue Gas)

The design feed rate for the proof-of-concept unit was 2,500 SCFM (standard conditions at 60°F and 14.696 psia) of flue gas. The design allowed feed rate turndown to 75% of design. The flue gas composition, as received from the boiler, is given in Table 4.1.

The flue gas supply conditions from the recirculating fan are:

- Pressure = 0 to +1 in. water column (WC)
- Temperature = 640°F to 690°F

4.2.2 Product(s)

The proof-of-concept unit was designed to yield treated flue gas and regeneration offgas whose composition is described below:

- Treated flue gas
 - 90 wt-% removal of SO₂ and NO_x.
 - 1.9 grains/dry SCF fly ash load and 90% efficiency
- Regeneration offgas; suitable for sulfur recovery or sulfuric acid manufacture

4.2.3 Process Conditions

The adsorber and regenerator process conditions are listed in Tables 4.2 and 4.3.

Table 4.2
Adsorber Process Conditions

<u>Variables</u>	<u>Nominal</u>	<u>Range</u>
Bed Temperature	750°F (note 1)	700°F min. to 800°F max.
Gas-Outlet Pressure	-28" H ₂ O	(note 2)
Bed Height	3 ft.	1.5 to 5.0 ft (note 3)
Bed Gas Velocity	4.5 fps	(note 4)
Sorbent Circulation Rate	5,500 lb/hr	1,860 to 5,500 lb/hr
Cu/S Mole Ratio	6 to 1	2 to 1 min. to 6 to 1 max.
NH ₃ /NO _x Mole Ratio	1.0	0.5 min. to 2.0 max. (note 5)
Sorbent Residence Time	15 minutes	10 to 30 minutes

Notes:

- ¹ Maximum absorber temperature may be limited by heat loss.
- ² Absorber pressure will vary with unit hydraulics.
- ³ Maximum bed height may be limited by station operations.
- ⁴ Superficial velocity determined at bed inlet conditions.
- ⁵ Maximum may be limited by breakthrough.

Table 4.3
Regenerator Process Conditions

<u>Variables</u>	<u>Nominal</u>	<u>Range</u>
Bed Temperature	850°F	800°F min. to 900°F max.
Operating Pressure	-5 " H ₂ O	(note 1)
Methane injection	42 lb/hr	28 min. to 84 max.
Sorbent Resid. time	60 minutes	30 to 90 (note 2)

Notes:

- ¹ Regenerator pressure will float with the absorber.
- ² Residence time is independent of circulation rate.

5.0 PROCESS DESCRIPTION

A simplified flow diagram is shown in Figure 5.1.

5.1 FLUE GAS ROUTING

5.1.1 Supply

The slipstream of flue gas from the host unit is taken from the discharge of the flue gas recirculating fans that control the temperature zones in the host boiler. Flue gas composition and temperature from this location is representative of the area where commercial flue gas treating would be anticipated. Taking the flue gas from the discharge of the recirculating fans provided a convenient take-off point from the host and also supplied the flue gas at a pressure that helped reduce the fan utilities required by the demonstration unit. The only drawback from this take-off point is that the fly ash load at this location is lower than it would be at the point where the commercial unit would be expected to be located. Fly ash injection could be performed to demonstrate the unit's ability to handle the fly ash.

5.1.2 Flue Gas Heating

The inclusion of a flue gas heater is required to heat the flue gas to the temperatures required in the absorber. The heater makes up for heat losses from the host unit and allows for variations in the absorber operating temperature. The flue gas heater is usually not required on a commercial scale unit unless the fluidized bed is located after the economizer.

Electric heating had originally been considered for this service because it would not affect the flue gas composition. However, high capital and operating costs made electric heating impractical. In-line fired heaters have been used successfully in other demonstration-scale units with success. Accounting for the flue gases created by this heater is accomplished by measuring the flow and composition of the incoming gas downstream of the heater.

FIGURE 5.1
PROCESS FLOW DIAGRAM OF 2,500 SCFM
UOP FLUIDIZED-BED COPPER OXIDE PROCESS

5.1.3 NH₃ Injection

The NH₃ injection point is located downstream of the inlet flue gas analyzer but far enough from the absorber to ensure good mixing before the flue gas contacts the circulating sorbent. The injection rate is based on the results of the data from the LCTU operation. The injection rate is variable on flow control. The nominal injection rate is based on 100% of theoretical to avoid any emissions problems associated with sending excess ammonia to the stack. Analyzers at the absorber outlet verify the efficiency of NO_x conversion.

5.1.4 Absorber

The use of a fluidized bed allows good solids and flue gas contacting and minimizes the flue gas pressure drop. The absorber grid distributes gas evenly to the sorbent bed and allows fly ash to pass through the grid and fluidized bed along with the flue gas.

5.1.5 Treated Flue Gas

The exiting flue gas is analyzed for SO₂ and NO_x to measure the absorber performance. An oxygen analyzer is included to initiate a safety shutdown in the event that the oxygen level of the flue gas supply increases to a point where remixing with the excess natural gas in the regenerator offgas might create a combustible mixture. A control butterfly valve in the flue gas going to the flue gas induced draft (ID) fan provides a means of reducing the unit throughput. Gases from the lock hopper/lift system and the regenerator offgas are remixed with the treated flue gas for return back to the host unit. The flue gas ID fan provides the head needed to boost the flue gas pressure for return to the main boiler air preheater.

5.2 CIRCULATING GAS

5.2.1 Circulating Gas Cooling

Circulating treated flue gas is used both for spent sorbent heatup and sorbent lifting. The gas must be cooled to bring the head requirements down to a reasonable level so that the proper compressor can be specified. The circulating gas exchanger and circulating gas cooler accomplish this.

5.2.2 Circulating Gas Boosting

The circulating gas is boosted in pressure with a Spencer turbine compressor. The circulating gas rate can be adjusted by a butterfly valve at the compressor inlet.

5.2.3 Circulating Gas Dust Collection

A dust collector is located on the discharge of the circulating gas compressor to remove fly ash that would otherwise be circulated into the absorber heat-up zone and carried down into the sorbent circulating loop. Keeping fly ash out of this area is important with respect to ball-valve wear and gas distribution in the absorber heat-up zone and regenerator.

5.2.4 Circulating Gas Reheating

The circulating gas is first reheated in an exchanger with the hot incoming slipstream of treated flue gas. It is then brought up to final temperature with the electric circulating gas heater. Heat input is controlled by the gas temperature to the absorber.

5.3 LIFT GAS

5.3.1 Lift Gas Boosting

Lift gas is taken as a slipstream from the circulating gas coming from the circulating gas dust collector. The lift gas compressor boosts the lift gas to the pressure required to accomplish the sorbent lifting.

Flow control on the outlet of the lift gas compressor satisfies the minimum flow requirements of the lift gas compressor. Lift gas is also used to pressure up the lock hopper to allow the transfer of sorbent to the lift engager.

5.3.2 Lift Gas Flow Control

The sorbent circulation rate is controlled by adjusting the relative rates of primary and secondary lift gas going to the lift engager. Secondary air is adjusted to get the desired sorbent circulation rate, and the primary air rate is adjusted to maintain the total lift gas rate required in the lift line.

5.4 NATURAL GAS HEAT-UP FOR REGENERATION

Natural gas (predominantly methane) is used as regeneration gas to reduce the copper sulfate and excess copper oxide on the spent sorbent in the regenerator. The regeneration gas is flow controlled from the natural gas heater to the regeneration gas heater. The temperature of the gas from the regeneration gas heater to the regenerator is controlled at a sufficient operating level to ensure efficient reaction and may be varied to help the heat balance of the regenerator.

5.5 REGENERATOR OFFGAS RETURN

The offgas from the regenerator leaves the regenerator on pressure control and is remixed with the treated flue gas for return to the host unit. Oxygen and excess methane levels are monitored for safety reasons. In the commercial unit, this stream of highly concentrated SO_2 is sent to downstream processing in a sulfur recovery unit.

5.6 SORBENT CIRCULATION

5.6.1 Fluidized Bed

Sorbent enters the fluidized bed via the lift line coming from the lift engager below. Upon exposure to the excess oxygen in the flue gas, the reduced copper is oxidized to the active CuO form for reaction with the SO_2 in the flue gas. The optimum level of the fluidized bed is a trade-off between

pressure drop, which relates to fan utilities, and residence time, which relates to the required sorbent circulation rate.

5.6.2 Sorbent Heat-up

Sorbent leaves the fluid bed either via the overflow risers or the bottom of the bed, depending on which mode of absorber level control is being used. To raise the sorbent temperature from 750°F in the absorber to 850°F in the regenerator, the sorbent is put in contact with the hot circulating gas in a countercurrent plug-flow fashion. The circulating gas leaving the heat-up zone exits through the riser in the absorber, where it mixes with the flue gas leaving the fluidized bed.

5.6.3 Absorber Buffer

The hot sorbent passes into the absorber buffer section, where flue gas is purged from the sorbent with an upward flow of nitrogen. The upward flow of buffer gas is assured by maintaining the absorber buffer pressure at 5 in. of H₂O pressure above the absorber. In a likewise manner, buffer gas flows downward into the regenerator along with the sorbent. Thus, the absorber heat-up zone outlet and the regenerator operate at the same pressure, with the absorber buffer operating at 5 in. of H₂O pressure above both vessels.

5.6.4 Sorbent Regeneration

Sorbent is regenerated in the plug-flow regenerator, where the sorbent comes in contact countercurrently with the upward flowing regeneration gas, methane. Gas flow is distributed by means of an annular distributor.

5.6.5 Sorbent Addition

To make up sorbent lost through attrition, fresh sorbent is added via the sorbent-addition lock hopper. The sorbent is added to the top of the regenerator after the lock hopper is purged of oxygen and the pressure is brought up to the operating pressure of the regenerator. As the fresh sorbent is added, it is brought up to the temperature of the regenerator bed by the regeneration gas and reduced before normal use in the absorber.

5.6.6 Lock Hopper

The main function of the lock hopper is to transfer sorbent from the regenerator (operating at 5 in. H₂O pressure) to the lift engager, (operating at 6 psig). The lock hopper cycles through four steps to accomplish the transfer of sorbent: pressure up, load, depressure, and unload.

The secondary function of the lock hopper is to provide isolation between the methane-rich regenerator section and the lift section, which uses flue gas as the lift media and can contain varying concentrations of oxygen.

5.6.7 Sorbent Lift

Sorbent lift from the bottom of the structure to the top of the absorber is accomplished with the lift engager. Although the lock hopper is bringing in sorbent batchwise, the lifting of the sorbent is continuous. A nuclear-level indication verifies that sorbent is both entering the lift engager and transferring to the absorber.

5.7 NITROGEN FLOWS

5.7.1 Regenerator

A small nitrogen purge is added to the sorbent outlet of the regenerator to purge regeneration gases upward. Additionally, nitrogen flow can be controlled to the regeneration heater for start-up and warm-up and also during normal operation for additional heat input to the regenerator.

5.7.2 Absorber

A small nitrogen purge is pressure controlled into the buffer area, a zone designed to split flow upward into the absorber and downward into the regenerator. This flow effectively keeps the oxygen atmosphere isolated from the methane atmosphere.

5.7.3 Safety Shutdown

When the controlled pressure differentials deviate to the point that purge flows may reverse, the isolation ball valves between the absorber and regenerator are closed, and a nitrogen purge is put on-line between the block valves to form a double block and purge. Similarly, the ball valves to and from the lock hopper are closed, and a nitrogen purge is put into the lock hopper.

5.8 CIRCULATING COOLING AIR FOR TEMPERATURE CONTROL

Circulating cooling air is controlled on the circulating gas cooler to ensure that the flue gas on the tube side does not drop below its acid dew point. The control of the flue gas temperature is required because of the large variation in ambient temperatures that will be encountered during the seasonal changes at the selected host site. A temperature controller on the flue gas leaving the cooler controls the discharge of the circulating cooling air. Fresh cool makeup air is made up on demand.

6.0 COMPONENT DESIGN BASIS

The process configuration consists of three primary components:

- Absorber
- Regenerator
- Sorbent transfer system

These sections have been incorporated into the proposed design to provide efficient flue gas treating with continuous sorbent regeneration.

The flue gas contaminant removal is accomplished in the fluidized-bed absorber. The fluidized-bed configuration provides intimate contact between the flue gas and sorbent and efficient heat distribution in the reaction zone.

The transfer of spent sorbent between the absorber and regenerator is accomplished by the solids transfer system using a lift gas. Natural gas is used to regenerate the sorbent in a moving-bed regenerator. Detailed project specifications for the 2,500 SCFM proof-of-concept unit were delivered to PETC earlier. The project specifications describe each individual piece of equipment, its size, material of construction, and other mechanical and process details. Piping and instrumentation information were also included in this report. None of this information is discussed in the following sections.

6.1 ABSORBER

6.1.1 Design Conditions

The design conditions for the absorber are 10 psig internal pressure at 1,000°F and 2.0 psig external pressure at 900°F. The killed carbon steel metallurgy is selected on the basis of conditions to be encountered in operation, optimal cost, and a short-life requirement of 1 year.

6.1.2 Fluidized Bed

The bed diameter of the absorber is essentially set by the superficial velocity of the flue gas required to keep the bed in the fluidized or ebulating regime. This velocity had been determined through pilot plant work in earlier phases as 4.5 ft/s. The design of the demonstration unit provides the flexibility to vary this velocity only to the extent that the flue gas rate can be turned up or down by the suction butterfly valve in the flue gas ID fan. The ability to vary the fluidized-bed velocity by varying the bed cross-sectional area was not deemed to be worthwhile when weighed against the costs and complication to the design. If feedback after operation indicates a need to study higher velocities, an inner sleeve could be added to achieve velocities as high as 10 ft/s.

The bed depth of the fluidized bed was nominally set at 3 ft. The design of the absorber allows an operating range of 1.5-5 ft. This fluidized-bed level is an important parameter of study because the effective residence time must be weighed against the utility costs associated with the drop in bed pressure. The drop in bed pressure is directly proportional to the fluidized-bed depth at about 5 in. of H₂O per foot of bed depth.

The residence time of the sorbent in the fluidized bed is not a directly adjusted operating variable because it is nominally set by the sorbent circulation rate and the criteria chosen for velocity and bed depth. A uniform residence time distribution for the sorbent particles is one of the main considerations in the design.

The design of the proof-of-concept unit has provisions for two modes of level control for the fluidized bed. The primary means of level control uses overflow pipes to control the sorbent level at a preset bed height. The chosen bed height is set by adjusting the overflow pipe height prior to the start of operation. An alternate means of controlling the fluidized-bed height is by using either the bed pressure differential or the nuclear level to sense the fluidized level and hence control the level by instructing the lock hopper to cycle. Sorbent is withdrawn directly from the bottom of the bed. Although the fluidized-bed level is more cyclic under this mode, withdrawal of the sorbent from the bottom of the fluidized bed may have advantages in terms of more uniform residence times for the sorbent pills in the fluidized bed.

6.1.3 Fluidized-Bed Grid

The fluidized-bed grid supports the fluidized bed and provides for uniform distribution of the entering flue gas. The support portion of the grid is a Johnson-type profile wire screen with wire orientation chosen to minimize fly ash blinding. The gas-distribution portion of the screen is a perforated plate designed for 2 in. of H_2O pressure drop. The basis for the grid pressure-drop selection is a trade-off between a value high enough to ensure flue gas distribution and a value low enough to give acceptable utility consumption. A nominal value of 15% of the bed drop was chosen for the distribution plate. The design of the plate is such that holes may be blanked off or added, as required.

6.1.4 Flue Gas Plenum

The flue gas plenum section allows the pressure of the lower heat-up zone to be near that of the top of the fluidized bed as opposed to the pressure of the incoming flue gas. This in itself is not important, but the differential of the circulating gas compressor would be unnecessarily high if the pressure drop through the dense heat-up bed was added to its differential. The flue gas plenum is thus operating at about -5 in. of H_2O gauge, with the heat-up zone pressure at about -22 in. of H_2O gauge.

The incoming flue gas is distributed over the cross-section of the absorber by a perforated plate at the flue gas inlet to the plenum. Although fly ash may build a heel in the plenum dead areas, the turbulence of the incoming flue gas will eventually carry the fly ash up through the grid and out the top of the absorber.

6.1.5 Sorbent Heat-up Zone

The sorbent heat-up zone raises the temperature of the spent sorbent from 750°F to the 850°F required in the regenerator. The heat-up is accomplished by contacting the circulating gas in a countercurrent fashion with the dense sorbent phase. The mass of circulating gas was determined by the heat-up duty required, given the maximum available temperature differential within the limits of the vessel metallurgy. The diameter of the gas heat-up zone was based on the annular distributor design. Also, the diameter of the heat-up zone limits the pressure drop through the dense bed to

prevent fluidization. The diameter of the gas heat-up zone turned out to be the same as the absorber. The geometry of the heat-up zone outlet along with the internal inverted outlet cone ensures that uniform plug flow of the dense sorbent phase is achieved.

6.1.6 Annular Distributor

The annular distributor is designed to uniformly distribute the heat-up gas across the cross-section of the heat-up zone without hindering the downward flow of sorbent. Limiting the gas velocity in both the incoming pipe and the annulus itself ensures good distribution without fluidizing the dense bed at the gas-sorbent interface. Computer-simulated streamline analyses predicts a uniform gas distribution.

6.1.7 Buffer Zone

The buffer zone is designed to provide isolation between the atmospheres in the absorber and regenerator. The pressure of the buffer zone is controlled at 5 in. of H_2O pressure above both the absorber and regenerator. This pressure results in a purging nitrogen flow upward into the absorber and downward into the regenerator. The length of the sorbent pipe into the buffer purge zone is designed so that the upward flow of nitrogen through the sorbent pipe breaks down the pressure differential between the buffer and absorber. A downward flow of nitrogen through the sorbent pipe to the regenerator breaks down the pressure differential between the buffer and regenerator.

6.1.8 Buffer Purge Zone

The purge portion of the buffer zone gives additional residence time for the purging of oxygen from the sorbent with nitrogen. The design purge time is based on two lock hopper volumes (four minutes) of purge. The design of the internals at the purge zone allows the upflowing nitrogen to be distributed across the purge volume by the internal annulus formed by the inverted cone containing the sorbent to be purged.

6.2 REGENERATOR

6.2.1 Design Conditions

The design conditions for the regenerator are 10 psig internal pressure at 1,000°F and 2.0 psig external pressure at 900°F. The killed carbon steel metallurgy is selected on the basis of conditions required, minimal cost, and a short-life requirement of 1 year.

6.2.2 Sorbent Inlet Pipe

The design of the sorbent inlet pipe allows the sorbent residence time in the regenerator to be changed by incrementally varying the length of the inlet pipe. Only when makeup sorbent is added will the sorbent level be above the angle of repose of the sorbent coming down the inlet pipe.

6.2.3 Sorbent Bed

The sorbent bed in the regenerator is the dense phase flowing downward and countercurrent to the upward flowing regeneration gas. The chosen regeneration bed dimensions are a balance between a length that would keep the structure height reasonable and a diameter small enough to ensure adequate vapor velocities and gas distribution.

6.2.4 Annular Distributor

The annular distributor in the regenerator was designed according to the same basic criteria as the annular distributor in the absorber.

6.2.5 Sorbent Outlet

The design for the sorbent outlet in the regenerator is similar to the absorber outlet. Ensuring that the dense sorbent phase flows through the regenerator is critical in achieving optimum regenerator efficiency. No plug flow in this vessel would result in a range of residence times. Some of the sorbent would have short residence time, and some would have long residence times. Both short and long residence times are undesirable.

6.3 SOLIDS TRANSFER SYSTEM

6.3.1 Lock Hopper

6.3.1.1 Design Conditions

The design conditions of the lock hopper are 50 psig internal pressure at 1,000°F and 2 psig external pressure at 800°F. These design conditions are based on the requirements of the swing in pressure between the pressure and depressure steps. Metallurgy is killed carbon steel.

6.3.1.2 Sizing

The lock hopper is sized to contain a volume of circulating sorbent equal to 2 min. at the design circulation rate. This time is the minimum required for the lock hopper to go through its complete cycle. Sizing the lock hopper for the shortest cycle time gives a closer approximation of continuous sorbent removal from the fluidized bed. This continuous-mode approximation occurs when sorbent withdrawal is controlled from the bottom of the fluidized bed. At lower sorbent circulation rates, the lock-hopper cycle time would lengthen because the volume of sorbent that loads into the lock hopper remains constant.

6.3.1.3 Cycle Time

At the design sorbent circulation rate, the lock hopper must be able to cycle through its four steps in the 2 min. cycle time. The major steps of load, pressure, unload, and depressure are allotted about 20 sec. each. Valve stroking time is limited to 5 sec. for each full-sized valve. No time was allotted for dust settling, although the lock hopper logic control system can be modified at lower sorbent circulation to allow more time for dust settling to extend the life of the ball-valve seats.

6.3.2 Lift Engager

6.3.2.1 Design Conditions

The design conditions for the lift engager are 35 psig internal pressure at 1,000°F. This design pressure allows the lift engager to be pressured up to clear a slumped lift line if necessary. Metallurgy is killed carbon steel.

6.3.2.2 Lift Pipes

The sorbent lift pipes are designed strictly on the basis of the gas velocities required to accomplish the dilute-phase lifting of the sorbent. The pipe schedules are selected to give the desired annular cross-sectional area and not for erosion protection as may be expected. Final field adjustments can be made in the gap between the inlet of the internal lift pipe and the outlet of the external primary air pipe. After final adjustment, no other adjustments are required.

6.3.2.3 Sizing of the Lift Engager

In the final design of the proof-of-concept unit, the lift engager replaces the surge hopper (used in the original 10,000 SCFM design) to act as the surge volume for the unit sorbent inventory. Although the lock hopper loads the lift engager batchwise, the average level of the lift engager is monitored in steady operation to determine the rate of sorbent attrition. Thus, the lift engager is designed to hold one drum of makeup sorbent in addition to the normal volume of sorbent from the lock hopper.

6.4 GENERAL DESIGN REQUIREMENTS FOR THE FLUE GAS HEATER

Design considerations for the flue gas heater are straightforward. Typical in-line direct-fired heaters of this size operate with about 50% excess air. A combustion air fan is required because the duct pressure is close to atmospheric pressure at the heater location. Fly ash plugging is the main consideration for the location and orientation of the heater and burner.

6.5 CIRCULATING GAS CIRCUIT

6.5.1 Circulating Gas Exchanger

The circulating gas exchanger is a vertical tubular exchanger with the hot, fly-ash-laden gas on the tubeside flowing downward. The cleaner shell side gas flows countercurrently upward through baffles to improve heat exchange. Allowable pressure drop on both hot and cold sides is minimized to keep down the head requirements on the circulating gas compressor. However, pressure must be high enough to ensure adequate gas velocities for heat transfer. Temperatures were chosen so that the cold gas temperature rise is about 80 to 85% of the cold-end approach.

6.5.2 Circulating Gas Cooler

The circulating gas cooler design is basically identical to the circulating gas exchanger except that tempered circulating air is used on the cold side. The circulating gas cooler is close coupled to the circulating gas exchanger to minimize inlet and outlet losses. The flue gas outlet temperature was kept at 350°F, which is 50°F above the estimated acid dew point of 300°F.

6.5.3 Circulating Gas Dust Collector

The circulating gas dust collector is a fabric baghouse with pulse-jet cleaning. Design pressure drop is 2 in. H₂O when clean and 5 in. H₂O when dirty. The design efficiency is 99% for particles 1 μ m and larger. The dust collector operating temperature is 430°F, which is near the upper design limit of a fabric bag. Sintered metal cartridge elements have been considered during the earlier conceptual development stage of the demonstration unit but were later eliminated to reduce capital costs.

6.6 GENERAL DESIGN REQUIREMENTS OF REGENERATION GAS HEATER

The regeneration gas heater is an electric heater capable of heating the incoming methane source (natural gas) up to 975°F. For normal operations, the heater helps heat balance the regenerator, which is influenced by varying heat losses because of changing ambient conditions. The design duty of the regeneration gas heater is based on unit heat-up requirements for starting up the unit with nitrogen before bringing in the flue gas. Nitrogen can be added to the regeneration gas during

normal operations to help increase the regenerator operating temperature, but the corresponding decrease in regeneration gas concentration might negate any conversion advantage gained with the increase in temperature.

6.7 INSULATION

The insulation thickness of the regenerator was increased to raise the regeneration temperature to 926°F. In addition, the flanges between the absorber heat-up zone and the regenerator were insulated.

7.0 PLANT LAYOUT AND CONFIGURATION

This section describes the factors and options considered during the evolution of the plant layout.

7.1 STACKED VERSUS SIDE BY SIDE

As the design of the proof-of-concept unit evolved, the pros and cons of a stacked versus side-by-side design were weighed. Some of the advantages of the stacked design disappeared with the elimination of the following features from the original design:

- The elutriator for fines removal
- The surge hopper for sorbent surge and storage during maintenance
- The regenerator Buffer for atmosphere isolation

The main difference between the two options is in the structure height and associated foundation requirements and the requirement of one versus two lift systems. Smaller plot space and a lower sorbent attrition rate associated with a single lift favored a stacked design.

7.2 ABSORBER VERSUS REGENERATOR ON TOP

Having decided to stack the absorber and regenerator, the pros and cons of their relative location had to be weighed. The advantages of putting the absorber on top were:

- Putting the regenerator at the bottom of the structure allows sorbent to be lifted into the absorber with flue gas.
- The pressure differentials for the buffer system would result in a slightly positive operating pressure in the regenerator. Locating the regenerator above the absorber would result in a negative operating pressure, which would be less safe if a leak of outside air into the hot regeneration gas atmosphere were to occur.

7.3 GENERAL LAYOUT

The general layout of the unit is basically set by the location of the primary vessels in the unit. Consideration is given to providing adequate expansion for gas and sorbent piping. The main consideration for the sorbent piping is minimizing the number of elbows in the lift line and the physical conditions that cause sorbent attrition. Such conditions include any sharp ledges or sudden discontinuities. For flow meters, the requirements of the upstream and downstream meter run dictate the location of some of the equipment. When location of equipment is not proscribed, maintenance considerations are considered.

Detailed plant layout drawings were included with the project specifications were submitted to PETC.

8.0 INSTRUMENTATION AND CONTROL

This and the next section discuss the general instrumentation, controllers, analyzers, and safety features included in the proof-of-concept unit design.

8.1 GENERAL INSTRUMENTATION

8.1.1 Digital Controllers

The general control instrumentation is based on a distributed control system (DCS). The digital controllers of the DCS are easily configured via the system software. An advantage of a DCS, especially in the development of a process unit design, is the ease with which software alarm points and instrument control loops and cascades can be reconfigured. This advantage will increase as experience is gained with the operation of the unit. All flow, temperature, and pressure indicators and controllers requiring a viewed output in the control room are part of the DCS instrumentation.

8.1.2 Analog Controllers

In the buffer differential pressure controllers, where a tight control and a fast response are required, analog instrumentation is specified. For critical alarms and shutdown systems, hard-wired shutdown circuits are used instead of software links that are less reliable and prone to nuisance shutdowns.

8.1.3 Critical Alarms and Shutdowns

Electrical signals for all shutdown circuits are hard wired and normally energized. To activate a shutdown circuit, the signal must be broken or deenergized. This restriction ensures that the shutdown system will be operational when needed and will shut down the equipment during power failures. Manual resets are used on shutdown circuits to prevent systems from coming back on line on their own when shutdown conditions return to normal.

8.2 PROGRAMMABLE LOGIC CONTROLLER

A programmable logic controller (PLC) is used to control and safeguard the sorbent circulation system. The semibatch operation of the lock hopper requires a significant amount of sequencing and verification, which are ideal applications for a PLC. The verification aspect of the PLC provides a degree of safety by shutting down the sorbent circulation and isolating atmospheres, if necessary, in the event that a valve is not verified closed or some other input is not satisfied.

8.3 ANALYZERS

A completed listing of all the analyzers is provided in Table 8.1.

8.3.1 SO₂ and NO_x

The SO₂ and NO_x analyzers are continuous on-line analyzers used to monitor unit performance. Concentrations are monitored at both the inlet and outlet of the absorber. The SO₂ concentration is also monitored on the regeneration gas leaving the regenerator.

8.3.2 Oxygen

Oxygen levels are monitored on the flue gas stream to and from the absorber and on the flue gas from the regenerator. The main purpose of the oxygen monitors is to ensure that the unit is not operated when the oxygen levels increase above the normal concentration of 3.2%.

8.3.3 Methane

The regeneration offgas from the regenerator is monitored for excess unreacted methane. The regeneration offgas will be remixed with the treated flue gas, and so the amount of excess methane must be monitored to ensure that concentrations never get above the explosion limits.

Table 8.1
Analytical Instrumentation
for Gas Analysis

<u>Location</u>	<u>Analysis</u>	<u>Range</u>	<u>Instrument</u>
Absorber In	SO ₂	0-4,000 ppm	UV, Continuous
	NO _x	0-1,000 ppm	Chemiluminescent, Continuous
	CO/CO ₂	--	Orsat
	O ₂	0-6%	Zirconia, Continuous
Absorber Out	SO ₂	0-400 ppm	UV, Continuous
	NO _x	0-100 ppm	Chemiluminescent, Continuous
	CO/CO ₂	--	Orsat
	O ₂	0-6%	Zirconia, Continuous
	NH ₃	--	UV, Continuous
Regenerator Out	SO ₂	0-25%	UV, Continuous
	CO/CO ₂	--	Orsat
	O ₂	0-10%	Paramagnetic, Continuous
	CH ₄	0-20%	IR, Continuous
Between Regenerator and Lift Engager	O ₂	0-6%	Zirconia, Continuous

9.0 SAFETY

9.1 GENERAL

9.1.1 Safety Equipment Specification

The general safety equipment includes eyewash and shower stations along with all equipments that are required for safe handling of the chemicals and sorbents.

9.1.2 Material Safety Data

The Material and Safety Data Sheets (MSDS) for the few chemicals, that are used in the process are readily available from the chemical manufacturers. Anhydrous ammonia and nitrogen are the only chemicals injected. The solid sorbent used in the process is nontoxic, and a MSDS for it is available from UOP.

9.2 ATMOSPHERE ISOLATION WITH BUFFERS

9.2.1 Absorber Buffer

The absorber buffer isolates the flue gas stream from the regenerator. The regenerator can have a significant concentration of methane depending on the regenerator efficiency and the amount of excess regeneration gas being injected. Although the flue gas is normally too lean in oxygen to form a flammable mixture with the methane, start-up or upset conditions in the main boiler can result in oxygen concentrations that may form a flammable mixture. The differentially controlled absorber buffer ensures that the atmospheres never mix by purging nitrogen in both directions away from the absorber buffer region. When the buffer pressure differential in either direction drops to the point at which a reversal of flow may occur, the logic control system shuts down sorbent circulation and isolates the absorber from the regenerator with double block valves and a nitrogen purge in between.

9.2.2 Regenerator Buffer

The lock hopper between the regenerator and lift engager is in effect a bubble that prevents mixing of the methane-rich atmosphere from the flue gas by ensuring that one set of double block valves is closed at all times. Also, having an upward nitrogen purge into the regenerator helps ensure that regeneration gas does not migrate downward into the lock hopper. The regenerator buffer zone was removed in the 2,500 SCFM design.

9.3 SHUTDOWN SYSTEMS

9.3.1 Host-Unit Main Shutdown Switch

All shutdown systems in the proof-of-concept unit are activated when a shutdown signal is received from Commonwealth Edison. The only exceptions are the circulating gas compressor and lift gas compressor.

9.3.2 Emergency Board and Field Shutdown Switches

All shutdown systems in the proof-of-concept unit are activated when either the board or field emergency run/stop pushbuttons are activated. The exceptions are the circulating gas compressor and lift gas compressor.

9.3.3 Flue Gas Heater

The flue gas heater shutdown system shuts off fuel gas to the flue gas heater under the following additional conditions:

- Low flue gas flow
- High flue gas heater outlet temperature
- Manual pushbutton board shutdown
- Any additional vendor-required shutdowns

9.3.4 Upper Isolation System

The upper isolation system isolates the sorbent line between the absorber buffer and regenerator under the following additional conditions:

- Upper isolation pushbutton is activated.
- The differential pressure (timed) between the absorber outlet and the absorber bubble is low.
- The differential pressure (timed) between the regenerator and the absorber bubble is low.

9.3.5 Lower Isolation System

The lower isolation system isolates the sorbent line between the regenerator and lift engager under the following additional conditions:

- Lower isolation pushbutton is activated.
- The nitrogen flow (timed) to the regenerator sorbent outlet is low.
- The instrument air pressure is low.

9.3.6 Regeneration Gas and Ammonia Injection

The natural gas flow to the regenerator and the ammonia flow to the absorber are shut down under the following conditions:

- Emergency stop switch tripped
- Regenerator gas pushbutton activated
- High regenerator pressure
- Upper isolation closed
- Lower isolation closed
- High regeneration heater outlet temperature

9.4 RELIEF VALVES

Relief valves protect individual vessels from overpressure resulting from isolation during operation. The absorber does not have a relief valve because it cannot be isolated from the main boiler (except by blinding for maintenance). The regenerator and lock hopper are susceptible to overpressure from the nitrogen header. The relief valves are located on the colder source of overpressure rather than directly on the hot vessel. Locating a valve on the hot vessel would require a high temperature relief valve design.

10.0 TEST STRATEGY

The objectives during operation and integrated testing of the proof-of-concept unit were to evaluate performance, identify important operating variables, optimize operation, and provide data for a conceptual design of the fluidized-bed flue gas treating process. The testing program consisted of separate subtasks:

- Test-plan development
- Unit shakedown
- Key process variables
- Process variable study
- Long-term reliability study
- Facility dismantling

10.1 TEST PLAN DEVELOPMENT

The objective of this task was to design a testing program to demonstrate the commercial and technical feasibility of the fluidized-bed copper oxide process. This sequence of tests was specifically designed to accomplish the overall objectives. Testing was to be conducted while operating in a continuous, integrated mode on a flue gas from the host utility.

The testing program would have required approximately 12 months of operation and would consist of two phases, each of six months' duration. These two phases are a process variable study and a long-term reliability study.

10.2 UNIT SHAKEDOWN

The test strategy anticipated that a four-week period of operating time would be required before process variable testing could begin. The initial operating conditions are:

- Absorber temperature of 740°F
- Sorbent circulation of 4,400 lb/hr
- Bed height of 3 ft
- Gas velocity of 4.5 ft/sec
- Regenerator temperature of 850°F

These conditions should be varied as necessary to test the operation of all process and analytical equipment.

During the initial operation, sorbent attrition measurements would be regularly determined. Start-up, shutdown, and emergency procedures would be evaluated. All instruments would be tested and recalibrated.

10.3 KEY PROCESS VARIABLES

The important operating variables in the copper oxide process are reviewed in this section. The testing program was designed to investigate as many of these variables as possible in the available time. Those variables that were believed to have the largest impact on the commercial potential of the process were given priority in the experimental design.

The rate of sorbent attrition and the effects of flue gas trace contaminants and fly ash on sorbent performance were to be determined. The absorber outlet gas would be monitored for unreacted ammonia, and the regenerator offgas would be monitored for unreacted reducing gas. All pertinent gas analyses are outlined in Table 8.1.

The important process variables are sorbent bed height, Cu/S mole ratio, adsorber temperature, NH_3/NO_x ratio, regenerator temperature and time, and flue gas constituents.

10.3.1 Sorbent Bed Height

The sorbent bed height would be controlled by varying the sorbent inventory in the absorber. The bed-height variable affects the gas residence time in the sorbent bed. Increasing the sorbent bed height will increase the gas residence time and, with all else held constant, result in an increase in SO_2 removal. Decreasing the sorbent bed height will decrease the gas residence time and, with all else held constant, result in a decrease in SO_2 removal.

The volumetric gas flow through the sorbent bed could be increased without decreasing the gas residence time if the sorbent bed height is increased at the same time. This change may affect the overall process economics. Because higher superficial velocities are allowed at the increased sorbent bed height, smaller equipment could be designed, and decreased capital costs could be realized. However, these changes may have an offsetting economic effect. The higher pressure

drop through the increased sorbent bed results in higher operating costs because the power requirements of the draft fan are greater. Trade-offs have to be made between the capital and operating costs resulting from adjustments to the sorbent bed height.

10.3.2 Cu/S Mole Ratio

The Cu/S mole ratio is defined as the moles of copper entering the absorber with the circulating sorbent divided by the moles of sulfur entering with the flue gas. The Cu/S mole ratio is controlled by adjusting the sorbent circulation rate. (This ratio assumes a constant sorbent copper loading, flue gas flow rate, and SO₂ concentration.) Decreasing the sorbent circulation rate decreases the Cu/S mole ratio and, with all else held constant, decreases the SO₂ removal.

Increased Cu/S mole ratios result in shorter sorbent residence times in the absorber, and so the overall process economics may be affected. With the increased Cu/S mole ratio, lower capital costs can be realized because the absorber size can be reduced. However, this increase can have an offsetting economic effect. The increased sorbent circulation rate results in higher sorbent attrition and higher operating costs. Trade-offs have to be made between the operating and capital costs resulting from adjustments to the Cu/S mole ratio.

10.3.3 Absorber Temperature

The absorber temperature would be controlled by adjusting the temperature of the flue gas entering the absorber. The inlet flue gas temperature can be changed by adjusting the firing rate of the burner placed in the flue gas duct upstream of the absorber. Increasing the absorber temperature, with all else held constant, would increase the SO₂ removal. Decreasing the absorber temperature, with all else held constant, would decrease the SO₂ removal.

Increasing the absorber temperature would increase the operating cost because of the higher fuel requirements for the flue gas in-line burner. However, the higher reactivity of the sorbent at the higher temperature could be used to reduce the Cu/S mole ratio or absorber size. Reduced Cu/S mole ratios lead to lower sorbent circulation rates and reduced operating cost through lower catalyst attrition. The smaller absorber size results in a lower capital cost. Trade-offs were to be made between the operating and capital costs resulting from adjustment to the absorber temperature.

10.3.4 NH₃/NO_x Ratio

The NH₃ would be injected into the flue gas line by a metering device upstream of the absorber. Increasing the NH₃/NO_x ratio, with all else held constant, would increase the NO_x removal. After a certain point, however, increasing the NH₃/NO_x ratio would not significantly improve the NO_x removal and will result in other problems. Unreacted NH₃, which breaks through the sorbent bed, would cause corrosion and plugging problems downstream of the absorber. In addition, operating costs are increased by the higher NH₃ use. The optimum NH₃/NO_x ratio was to be determined at different absorber operating conditions.

10.3.5 Regenerator Temperature and Time

The regenerator temperature would be controlled by heating the sorbent entering the regenerator vessel with hot, treated flue gas. Higher regenerator temperatures would allow shorter sorbent residence times in the regenerator at the same regeneration efficiency. The higher operating costs associated with the higher regenerator temperatures were traded off with the lower capital costs associated with shorter sorbent residence times.

10.3.6 Flue Gas Constituents

Trace elements in the flue gas may result in the loss of sorbent activity over a long period of operation. This effect, if it exists, was to be determined during the testing program. In addition, although fly ash deactivating the sorbent had not been an issue previously, this possibility would be investigated over an extended test period.

10.4 PROCESS VARIABLE STUDY

The objective of this task was to evaluate the performance, identify important operating variables, determine the interaction of these variables, and optimize the operation of the proof-of-concept facility. The process variable study would consist of:

- Determination of the effects of the operating variables on the regeneration section
- A set of experiments to determine the process system response to varying several important operating variables. (These variables are defined below.)

10.4.1 Variables

To design a useful experimental program, each of the relevant variables, and their interactions with one another, must be understood. As a starting point, each variable is defined as being independent or dependent on changes to other variables. The following independent variables were investigated in the proposed experimental program:

- Absorber
 - Bed temperature
 - Sorbent circulation rate
 - Sorbent bed height
- Regenerator
 - Bed temperature
 - Sorbent residence time

Assuming that the flue gas volumetric flow rate, contaminant levels, and sorbent copper loading remain constant, the following are the dependent variables:

- Absorber
 - Gas residence time in absorber
 - Sorbent residence time in absorber
 - Sorbent attrition rate
- Regenerator
 - Gas residence time in regenerator
 - Sorbent attrition rate

The independent variables are adjusted to optimize (minimize) the operating cost. Constraints are the achievement of 90% removal of both SO_2 and NO_x contaminants from the flue gas stream.

The effects of varying the NH_3/NO_x ratios would also be investigated. However, this variable was evaluated separately from the independent variables.

10.4.2 Regenerator Experimental Plan

The following process variable matrix defines the proposed experimental plan for the regenerator. The matrix was defined by the following three sets of independent variables:

- Bed temperature, °F: 800, 850, 900
- Residence time, min: 30, 60, 90

All combinations of these two independent variables would be tested in 9 experiments. The regenerated sorbent would be analyzed for S, Cu, SO_4^{2-} concentration at each condition. During the regeneration testing, the spent condition of the inlet sorbent must remain constant. Therefore, the absorber would be run at the same operating conditions during this testing period.

The regenerator study would be conducted to identify the operating conditions required to decouple the regenerator operation from the absorber operation. For the absorber process variable study, the sorbent must always have the same properties when leaving the regenerator and entering the absorber. The sorbent must be regenerated to the same extent regardless of its sulfur-loaded condition when it enters the regenerator. The operating conditions selected for the regenerator would be held constant during the absorber process variable study and be more severe than those required at the lower sulfur loading levels.

10.4.3 Absorber Experimental Plan

The independent process variables to be considered in this initial study include:

- Sorbent bed height (ft.): Controlled by varying the sorbent inventory in the absorber (2,3,6)
- Sorbent circulation rate (lb/hr): 1,800, 4,400, 5,500
- Absorber temperature (°F): 700, 750, 800

The values indicated for these variables were based on the experimental results obtained from the LCTU operation and the final form of the proof-of-concept facility.

With these independent variables established, parameters that describe the system can be defined from an engineering viewpoint. These independent variables are:

- Gas residence time (sec)
- Sorbent residence time (sec)
- Cu/S mole ratio

Finally, the dependent variables for the system are:

- SO₂ removal
- NO_x removal
- Sorbent attrition

As an example, some of the experimental conditions are listed in Table 10.1.

Table 10.1
Experimental Conditions

<u>Test No.</u>	<u>Superficial Gas Velocity, (ft/sec)</u>	<u>Sorbent Bed Height, ft</u>	<u>Sorbent Circulation Rate, lb/hr</u>	<u>Absorber Temperature, °F</u>
1	4.5	3	1,800	700
2	4.5	3	5,500	700
3	4.5	3	1,800	800
4	4.5	3	5,500	800
5	4.5	3	4,400	750
6	4.5	2	1,800	750
7	4.5	6	1,800	750
8	4.5	2	5,500	750
9	4.5	6	5,500	750
10	4.5	3	4,400	750
11	4.5	2	4,400	700
12	4.5	6	4,400	700
13	4.5	2	4,400	800
14	4.5	6	4,400	800
15	4.5	3	4,400	750

The base conditions (Test Nos. 5, 10, 15) should be run in the center of each block of experiments. The 9 regenerator experiments would be conducted at these absorber base conditions. Based on the results of this initial program, particular follow-up experiments could be formulated to provide data in the areas of most interest.

10.4.4 Other Absorber Experiments

Following the designed experiment and any follow-up required, the next phase of the variable study would determine the effects of changes in the NH_3/NO_x ratio. If higher superficial flue gas velocity effects may be studied, the experimental program would have to be expanded. Lower velocities can easily be achieved by using the control valve. Higher velocities require modification of absorber geometry.

The NH_3/NO_x ratio would be varied over the range of interest determined in the LCTU testing program. The key information to be obtained was the extent of ammonia breakthrough into the treated flue gas.

10.5 SCHEDULE

The number of days allotted for experiments proposed in this program is listed below:

	<u>Days</u>
Process variable (regenerator)	19
Process variable (absorber, initial)	51
Process variable (absorber, follow-up)	33
NH_3/NO_x	14
Absorber geometry	30
Recheck	<u>7</u>
Total	154

The experiments were periodically rechecked to determine if any long-term sorbent deactivation had occurred during the experimental program. This retesting of the sorbent's performance must occur at specified base conditions.

Because of the developmental nature of the program, the time allotted for each experiment was quite conservative. Time frames were determined to allow for support tasks such as sorbent loading, maintenance, and host utility interaction. Because SO_2 and NO_x concentrations from the absorber would be constantly monitored, steady-state conditions would be easily achieved. Each test would be conducted over 16 hours of steady-state operation in the absorber. An 8-hour line-out period in between tests would allow sufficient time for complete inventory turnover in the absorber.

The regenerator was sized to provide one complete inventory turnover in approximately 60 minutes. Therefore, an 8-hour line-out period would be sufficient to reach steady state.

10.6 RELIABILITY TEST

The objective of this task was to assess the overall system reliability over a period of approximately six months. The long-term reliability test would simulate the periodic changes in gas-flow rates, which are characteristic of utility boiler operation. This load following and turndown operation would be run to demonstrate the ability of this process to provide consistent SO_2 and NO_x removal efficiencies under a simulated utility operating environment. Load following would be accomplished primarily by varying the sorbent circulation rate and NH_3 injection as required to maintain satisfactory efficiencies for contaminant's removal.

The reliability test would begin with a fresh load of sorbent. During the initial operation, attrition would be measured daily. This measurement would determine if an initially high level of sorbent attrition occurred with a fresh batch of catalyst. After the sorbent attrition rate had stabilized, sorbent attrition would be measured approximately once each week.

Sorbent characteristics would be analyzed during the course of the reliability test. Of primary interest would be the surface area, copper distribution, and trace contaminant levels on the regenerated sorbent. Any indications of sorbent deactivation as a result of poisoning by fly ash or trace contaminants would be noted.

Corrosion, erosion, and fouling of process equipment would be assessed during the reliability test. In addition, the long-term effects of attrited sorbent material on particulate collection devices would be evaluated. Safe disposal procedures for fly ash from the combustor would be established.

10.7 FACILITY DISMANTLING

Upon completion of the proof-of-concept test program, UOP would arrange for the dismantling of the installation and the disposal of equipment in accordance with contractual arrangements made with the subcontractor. UOP had planned to dismantle the unit to individual modules and ship the modules as per DOE instructions.

UOP's subcontractor would have completed this work, and the utility site would have been returned to its original condition. This work would include removal and disposal of foundations, piping, and other temporary facilities as well as general site cleanup.

11.0 UNIT OPERATING PROCEDURES

This section is a general description and procedure for start-up and shutdown of the 2,500 SCFM fluidized-bed copper oxide process unit to be installed at the Commonwealth Edison station at Kincaid, Illinois.

11.1 UNIT DESCRIPTION

The unit consists of three major sections: a fluidized-bed absorber, the sorbent regenerator, and the sorbent transfer section. Each section is briefly described before the start-up and shutdown procedures are outlined.

11.1.1 Absorber

The absorber contains a fluidized bed of CuO sorbent through which the untreated flue gas flows. The gas taken from the Commonwealth Edison flue gas duct at the outlet of the recirculation fan, is heated to 750°F, and enters the absorber at the bottom of the fluidized bed. The NH_3 is mixed with the flue gas at the inlet of the absorber for the reduction and removal of NO_x . The gas flows upward through the bed and exits at the top of the absorber and returns to the Commonwealth Edison duct system at the air preheater outlet. The absorber contains a profile wire screen grid with downcomers to allow sorbent to flow downward from the fluidized bed to the dense-phase heat-up zone. Gas flowing through the perforated plate at high velocity creates the fluidized bed. Regenerated sorbent enters the absorber through a standpipe with the outlet above the fluidized bed.

11.1.2 Regenerator

Sorbent flows by gravity from the absorber into the sorbent regenerator and from the regenerator to the sorbent transport system. The sorbent is regenerated using heated methane gas, which is injected at the bottom of the regenerator and flows up through the sorbent bed. Regeneration gas exits the top of the regenerator, is sent to the flue gas ID fan, and is then returned to the Commonwealth Edison duct system at the air preheater outlet.

11.1.3 Sorbent Transfer System

The sorbent flows by gravity to the sorbent transfer system, which consists of the sorbent lock hopper and the sorbent lift engager. The system is used to transfer regenerated sorbent from the bottom of the regenerator to the top of the absorber. The circulation rate was controlled by altering the operating conditions in the lift engager. The lock hopper can be used as a backup device to set the sorbent circulation rate while the lift engager accomplishes the sorbent lift and takes any sorbent volume surge resulting from fluctuations of the circulation rate. Sorbent lift is accomplished using the lift gas compressor.

Other major pieces of equipment in the unit are the flue gas heater, regeneration gas heater, circulating gas heater, circulation gas exchanger, circulating gas compressor, circulating gas dust collector, and circulating gas cooling fan. The purpose and operation of each piece of equipment will be covered in the detailed operating instructions.

11.2 UNIT PRECOMMISSIONING AND START-UP

The following start-up and shutdown procedures are general in nature and cover only the major steps to be taken during these activities. Detailed procedures would be written by the UOP Technical Service group as the unit was built and checked out prior to start-up.

11.2.1 Unit Checkout

The unit would be precommissioned in accordance with normal UOP procedures. Lines would be checked and cleaned of any construction debris and closed for leak testing. All lines and vessels would be checked to ensure that they are in accordance with the UOP drawings. Instrumentation would be checked for proper installation and calibration. The unit rotary equipment would be checked to ensure proper operation prior to unit start-up.

11.2.2 Sorbent Addition

Once the unit was checked out and readied for commissioning, the sorbent would be inventoried. The sorbent would be loaded into the system through the sorbent addition system at the top of the

regenerator and through the manway at the top of the absorber. The regenerator vessel should be loaded first. Once the system was loaded with the specified amount of sorbent, the unit would be ready for the start of gas and sorbent circulation.

11.2.3 Warm Up and Circulation

Air would need to be removed from the regenerator by using nitrogen from the nitrogen vaporizer. A small bleed of nitrogen would be left on the regenerator to maintain an air-free vessel. Gas circulation in the absorber would be started using air via the circulating gas compressors and start-up circulation lines. At this point the circulating gas heater and flue gas heater would be started to begin warming the absorber system.

The purpose of the start-up circulation lines is to warm up as much of the dead flue gas inlet and return lines as possible. This procedure prevents or minimizes any condensation that might occur when flue gas is introduced into the system. At the same time, a small stream of nitrogen can be sent through the regeneration gas heater to the regenerator to initiate heat-up of the regenerator and the sorbent.

Once the absorber gas is warm enough to start the lift gas compressor (effectively reducing its density to minimize starting loads), the sorbent circulation system can be commissioned. Line-out sorbent circulates at a steady rate. During these operations, instrumentation and safety systems, such as the isolation bubbles between the absorber and regenerator, are checked and put into service. The sorbent circulation rate is increased to the specified level, and the circulating sorbent temperature is increased. The system should be increased to a minimum temperature of 450°F to prevent acid condensation from the flue gas. At that point, the heaters should be shut down and gas circulation stopped to remove flue gas inlet and outlet isolation blinds.

11.2.4 Flue Gas to Absorber

Gas and sorbent circulation would be restarted. The heaters would be switched on to line out the temperature at 450°F. At that temperature, the flue gas can be charged to the absorber and the start-up circulation lines closed. At this time, the on-line analyzers and laboratory analysis can be commissioned to establish unit base conditions. The flue gas flow and inlet temperature would be

increased to the design value. The flue gas inlet temperature should line out at 750°F to ensure that ammonium salts would not be formed and deposited inside the vessel or lines. Only then would ammonia injection to the flue gas feed line be started. At this point, catalyst regeneration should be started by injection of the regeneration gas, methane. The regeneration gas heater would be used to increase the gas temperature to the design value.

Design conditions would be established throughout the unit, and routine operations and data collection would be started.

11.3 UNIT SHUTDOWN

The specific shutdown procedure would be dictated by the reason for the shutdown and the planned length of the shutdown. Additionally, specific considerations would be given to planned operations during the shutdown.

11.3.1 Routine Shutdown

The routine shutdown procedure would be carried out to stop the absorber reactions, reduce the system temperature, and purge the unit. This shutdown is accomplished by the following steps:

1. Stop injection of NH_3 to the absorber.
2. Reduce system temperature to 450°F.
3. Stop circulation of gas and swing the isolation blind to stop flue gas coming into the unit.
4. Continue gas circulation by making up gas with nitrogen to purge the unit of flue gas. Start purging the regenerator with nitrogen at this time.
5. Continue to reduce the system temperature by shutting down the system heaters.
6. Stop the lift gas compressors and the sorbent circulation when the temperature is low enough.
7. Stop the nitrogen flow once the regeneration unit is purged.
8. Continue circulating gas until the system is cool and ready for planned operations.
9. Make sure that all isolation blinds are in place and all vessels are purged with air to make them safe for vessel entry.

11.3.2 Emergency Shutdown

The following is a list of conditions that may cause a complete or partial shutdown of the unit. The reason for shutdown may be related to safety or protection of the equipment.

- Loss of the safety isolation bubble between the absorber and regenerator
- High temperatures of flue gas, circulating gas, sorbent lift gas, or any of the associated heaters, exchangers, or compressors
- Low flow of the flue gas or regeneration gas
- Low pressure differential between absorber and regenerator or high regenerator pressure
- Low pressure on the suction of the lift gas compressor
- Activation of vendor-supplied compressor or heater shutdown systems

Each emergency shutdown situation would require a specific set of operational responses, which would be detailed in the operating manual.

REFERENCES

1. D. H. McCrea, A. J. Forney, and J. G. Myers, "Recovery of Sulfur from Glue Gases Using a Copper Oxide Absorbent," Journal of the Air Pollution Control Association, Vol. 20, No. 12, (1970).
2. A. E. Arneson, F. M. Nooy, and J. B. Pohlenz, "The Shell FGD Process: Pilot Plant Experience at Tampa Electric," Fourth Symposium on Flue Gas Desulfurization, Environmental Protection Agency, Hollywood, FL, Nov., 1977.
3. A. O. Braun and J. B. Pohlenz, "Shell NO_x/SO₂ Flue Gas Treatment Process: Pilot Plant Evaluation," EPA Report 600/7-83/048, Sept., 1983.
4. J. P. Strakey, E. R. Bauer, and W. P. Haynes, "Removal of SO₂ and NO_x from Flue Gas in a Fluidized-Bed Copper Oxide Process," presented at the Sixth National Conference on Energy and the Environment, Pittsburgh, PA, May 21-24, 1979.
5. J. T. Yeh, R. J. Demski, J. P. Strakey, and J. I. Joubert, "PETC Fluidized-Bed Copper Oxide Process for Combined SO₂/NO_x Removal from Flue Gas," presented at the American Institute of Chemical Engineers Winter National Meeting, Atlanta, GA, March 11-14, 1984.
6. J. Ratalia-Brown and R. L. Hershey, "Technical and Economic Evaluation of the Fluidized-Bed Copper Oxide Flue Gas Treatment Process and Integrated Sulfur Producing Plants," prepared by Scientific Management Corporation for Mr. James Joubert of the Pittsburgh Energy Technology Center, June 1983.
7. A. R. Plantz, C. J. Drummond, and S. W. Hedges, "Performance of the Fluidized-Bed Copper Oxide Process in an Integrated Test Facility," presented at the 79th Annual Meeting and Exhibition of the Air Pollution Control Association, Minneapolis, MN, June 22-27, 1986.
8. R. R. Williamson, J. A. Morici, and T. L. LaCosse, "Phase I-Sorbent Life Cycle Testing: Fluidized-Bed Copper Oxide Process," prepared by UOP for the Pittsburgh Energy Technology Center under DOE Contract DE-AC22-85PC81004, Apr., 1987.
9. J. C. McArdle, D. G. Leshock, and R. R. Williamson, "Sorbent Life Cycle Testing: Fluidized-Bed Copper Oxide Process," presented at the Third Annual DOE Contractor's Review Conference on Coal Utilization and Environmental Control, Pittsburgh, PA, July 7-9, 1987.
10. P. P. Shah and D. G. Leshock, "Sorbent Life-Cycle Testing: Fluidized-Bed Copper Oxide Process," presented at the EPRI Fourth Symposium on Integrated Environmental Control, Washington DC, Mar. 2-4, 1988.

*CCR and Platforming are trademarks and/or service marks of UOP.

END

**DATE
FILMED**

4 / 10 / 92