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THE DESIGN OF A DRY, REGENERATIVE FLUIDIZED-BED COPPER OXIDE PROCESS FOR THE REMOVAL OF SULFUR DIOXIDE AND NITROGEN OXIDES FROM COAL-FIRED BOILERS

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ABSTRACT

The Fluidized-Bed Copper Oxide Process is an innovative and economical regenerative process for the simultaneous removal of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from the flue gas of coal-fired boilers. This process has been under investigation at the Pittsburgh Energy Technology Center of the U. S. Department of Energy, proceeding through various stages of development from bench-scale experimentation to operation of a large fluidized bed treating 1300 scfm of flue gas from a coal-fired combustor. A conceptual design for application of the process to a coal-fired power plant is evaluated based on reaction kinetics data, operating experience obtained during the development phase, and design studies that were performed in parallel with the process development. An economic evaluation of the process is also made based on the conceptual design for a 500-MW electric power generating facility.

INTRODUCTION

The application of flue gas desulfurization (FGD) technology to electric power generating plants has evolved over the past ten years to a state where reliable processes now exist that can obtain 90 percent removal of sulfur dioxide. However, while over one hundred flue gas cleanup processes have been evaluated experimentally, only wet lime/limestone slurry (throwaway) processes have

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achieved extensive application in the utility market. Spray drying continues to be the only commercially used "dry" flue gas FGD process, but it is being used exclusively at plants burning low-sulfur coal even though its applicability to high-sulfur coal burning plants has been proven. While these processes have finally proven successful, they are expensive to build and operate, and require the disposal of large quantities of waste product; this provides an incentive for developing less expensive alternatives.

The primary reason for the limited success of alternative cleanup processes is the stringent economic limitations placed on the technology by the large volumes of flue gas that must be treated. To compete with the established scrubbing technologies, developing processes must simply and reliably process these large volumes of flue gas at less cost while reducing or eliminating the waste material generated by limestone scrubbing and spray drying. In addition, regulations may be passed at some time in the future that will require electric power generating facilities to reduce nitrogen oxides emissions or that will provide for some type of credit for the removal of nitrogen oxides from flue gas. It is advantageous, therefore, that the developing alternatives for flue gas cleanup technology be capable of combined sulfur dioxide and nitrogen oxides removal.

The Fluidized-Bed Copper Oxide Process developed at the Pittsburgh Energy Technology Center is a promising new technology capable of removing greater than 90 percent of both the sulfur dioxide and nitrogen oxides present in the flue gas of coal-fired electric power generating facilities. In this process, the flue gas intimately contacts sorbent spheres in a fluidized-bed environment for less than one second. During this short duration contact, sulfur dioxide is reacted with the sorbent, and nitrogen oxides are selectively reduced to nitrogen and water by the addition of ammonia to the flue gas. It is a regenerative process that produces no waste products, making either elemental sulfur or sulfuric acid from the sulfur dioxide removed from the flue gas. The process operates at temperatures found before the air preheater of a coal-fired boiler, providing increased boiler efficiency by raising the flue gas temperature entering the air heater and by permitting lower flue gas temperatures at the exit of the air preheater without fear of corrosion by acid condensation. The

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

Fluidized-Bed Copper Oxide Process has the potential to provide an alternative to conventional scrubbing for control of sulfur dioxide as well as nitrogen oxides.

PROCESS DESCRIPTION AND DEVELOPMENT BACKGROUND

The sulfation of copper oxide and the catalytic reduction of nitrogen oxides in the presence of ammonia form the basis of the development of the Fluidized-Bed Copper Oxide Process. In 1970, McCrea et al.¹ described a sorbent that they prepared by impregnating a copper salt into a 1/16-inch alumina catalyst support. Bench-scale evaluations using a fixed-bed apparatus demonstrated that this mixed metal oxide sorbent material absorbed sulfur dioxide at temperatures ranging from 570°F to 800°F and that the spent sorbent could be regenerated with hydrogen or methane (natural gas), producing a concentrated stream of sulfur dioxide that could be converted to a sulfur by-product.

The use of copper-impregnated alumina spheres in a fluidized bed for the simultaneous removal of sulfur dioxide and nitrogen oxides from flue gas was first reported by Strakey et al.² in 1979. Additional information regarding the investigation was reported by Demski et al.³ In this investigation, a 6-inch-diameter fluidized-bed absorber was used to contact sorbent spheres (impregnated with approximately 5 weight percent copper) with the combustion products of natural gas containing added sulfur dioxide to obtain a concentration of 3000 ppm (volume). Ammonia was also added to the natural gas being burned, providing 800 ppm (volume) nitrogen oxides in the flue gas. The sulfur absorption capacity of the sorbent used was determined over 75 cycles of absorption and regeneration; results showed that 90-95 percent sulfur dioxide and greater than 97 percent nitrogen oxides removal could be achieved with an expanded bed height of 36 inches at a bed temperature of 752°F (400°C) while injecting ammonia in the flue gas for the catalytic reduction reaction. Because of the successful nature of these tests, additional work was performed to evaluate the following: a determination of the effect of NH_3/NO_x molar ratio on the simultaneous removal of sulfur dioxide and nitrogen oxides; measurement of unreacted ammonia (ammonia "slip") in the flue gas leaving the absorber; in situ measurements of sorbent attrition occurring in the fluidized bed; and an evaluation of the effect of fly ash addition on reactor performance.³

Based on these previous tests, as well as on a chemical reaction kinetics model developed using a microbalance reactor,⁴ the process concept was investigated at a larger scale using flue gas from the combustion of coal. A schematic of the 500 lb/hr coal combustion test facility used in these tests is shown in Figure 1. The results of this investigation are described in detail by Yeh et al.⁵ During these tests, the copper-impregnated alumina spheres containing approximately 5 weight percent copper were contacted with flue gas in a fluidized-bed absorber having a rectangular cross-section measuring 40 inches by 48 inches that allowed operation at expanded-bed heights of 18 inches, 36 inches, and 46 inches. A pictorial view of the absorber is shown in Figure 2. A flue gas flow rate of 1300 scfm (1 atm, 32°F) was produced for these tests from the combustion of bituminous coal containing 3 percent sulfur. The temperature of the fluidized bed was varied from 660°F to 900°F to simulate the load following conditions associated with a power plant. The sorbent flowed continuously through the fluidized-bed absorber and was collected over the duration of a run for regeneration in a packed-bed, batch regenerator measuring 2.5 ft in diameter by 26 ft high. Regeneration was accomplished using methane or mixtures of methane and hydrogen at a temperature of about 788°F (420°C). The sorbent material was regenerated sufficiently to leave only one weight percent of residual sulfur.

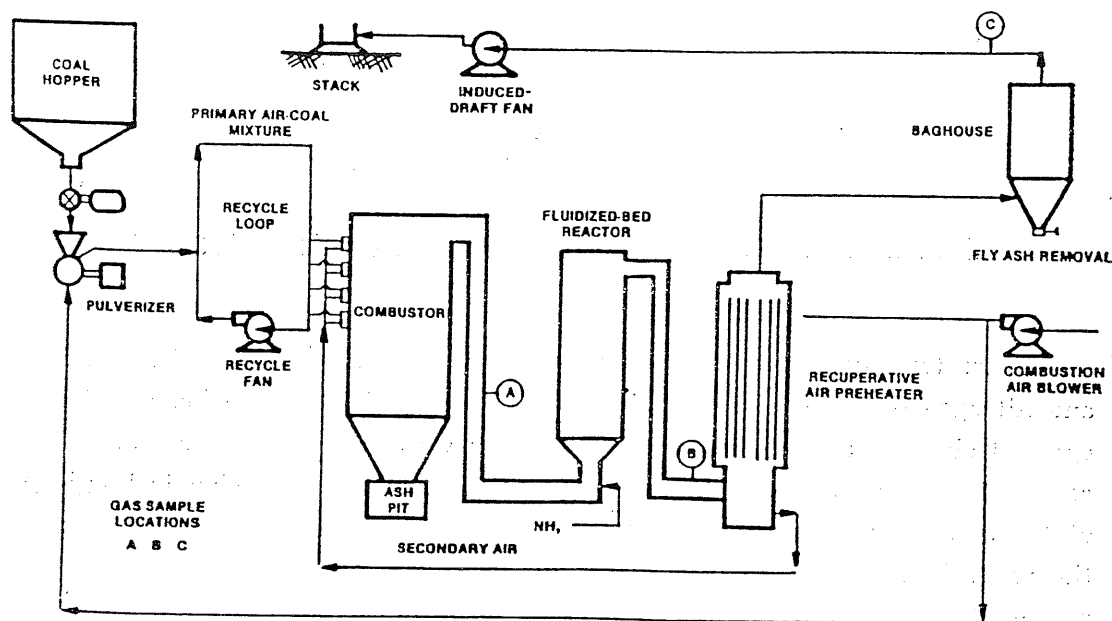


FIGURE 1. SIMPLIFIED FLOW SHEET OF 500 lb/hr (226.8 kg/hr) COMBUSTION TEST FACILITY

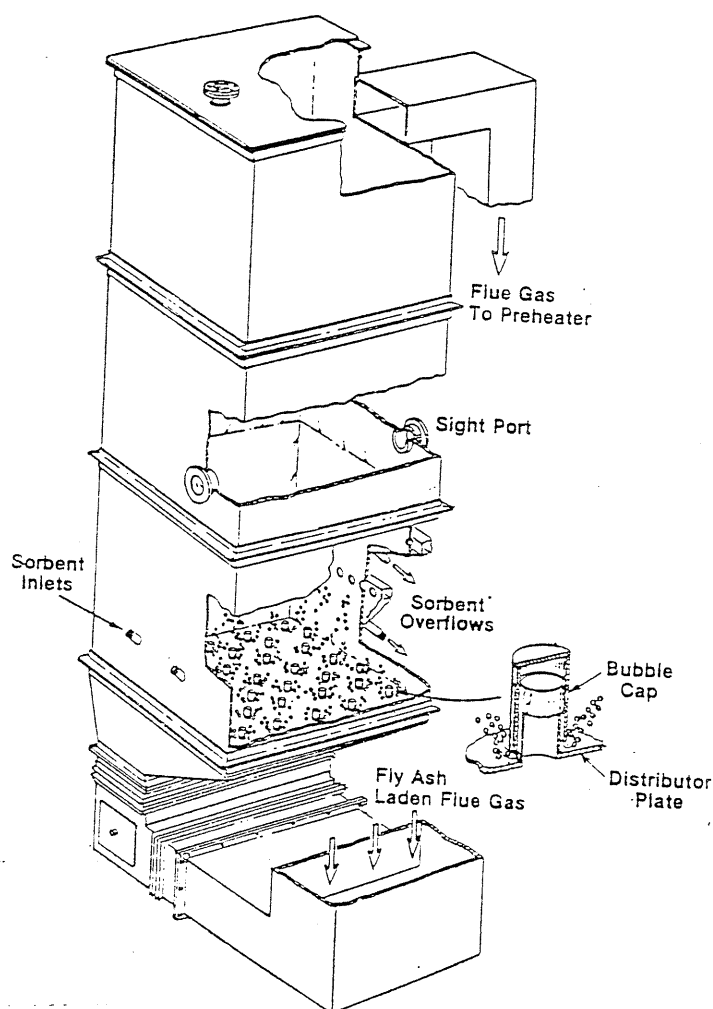


FIGURE 2. FLUIDIZED-BED ABSORBER (3'4"×4'0"×12'0")

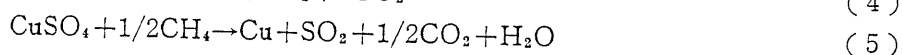
These tests demonstrated that 90 percent removal of both sulfur dioxide and nitrogen oxides could be achieved in a large fluidized bed of copper-impregnated alumina spheres in the presence of fly ash and other products of the combustion of coal. There was no measurable reduction in the chemical activity of the sorbent material after 24 cycles of absorption and regeneration during the tests. There were no observed adverse effects caused by increasing the cross-sectional area of the bed by a factor of 60 in scaling up from the 6-inch-diameter reactor used earlier.

PROCESS CHEMISTRY AND REACTION KINETICS

The chemistry of the reactions resulting in the removal of sulfur dioxides and nitrogen oxides from flue gas using copper-impregnated alumina spheres is described as follows. During sulfation, SO_2 and SO_3 in the flue gas react with the copper oxide on an alumina sphere:



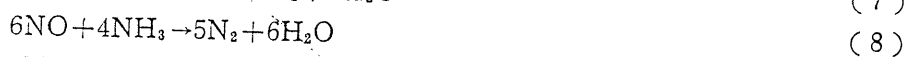
Regeneration of the sulfated sorbent can be accomplished in the presence of either hydrogen, carbon monoxide, or methane (natural gas):



The copper formed in the presence of the reducing gas is immediately oxidized to copper oxide upon contact with the flue gas:



Both copper oxide and copper sulfate act as catalysts for the selective catalytic reduction of nitrogen oxides in the fluidized bed, but copper sulfate is the more important of the two catalysts. Ammonia must be injected into the flue gas before the fluidized-bed absorber in approximately stoichiometric or slightly substoichiometric amounts to achieve 90 percent removal of nitrogen oxides.



Sulfur dioxide absorption and regeneration kinetics were determined for copper-impregnated alumina spheres by Yeh et al.⁴ The sulfation reaction was determined to be first order with respect to both the concentration of sulfur dioxide in the flue gas and the concentration of unreacted copper oxide. It was also determined that the rate of absorption of sulfur dioxide was not significantly affected by reaction temperature between 660°F and 840°F.⁴

Regeneration of the spent sorbent was investigated with either hydrogen, natural gas, or mixtures of hydrogen and carbon monoxide (synthesis gas) used as a reductant. The regeneration reaction was also found to be first order with

respect to reducing gas concentration for all of the reductants studied. It was also determined that the order of the regeneration reaction with respect to unreacted copper sulfate varied with the reducing gas used, as described below.

- Regeneration with natural gas—first order with respect to unreacted CuSO_4 .
- Regeneration with 2:1 CO/H_2 mixture—2.6 to 3.2 order of reaction with respect to unreacted CuSO_4 .
- Regeneration with hydrogen—3.1 to 4.0 order of reaction with respect to unreacted CuSO_4 .

Therefore, at any specified temperature, the rate of the regeneration reaction is substantially faster with hydrogen and mixtures of hydrogen and carbon monoxide than with natural gas (see Figure 3). In addition, the natural-

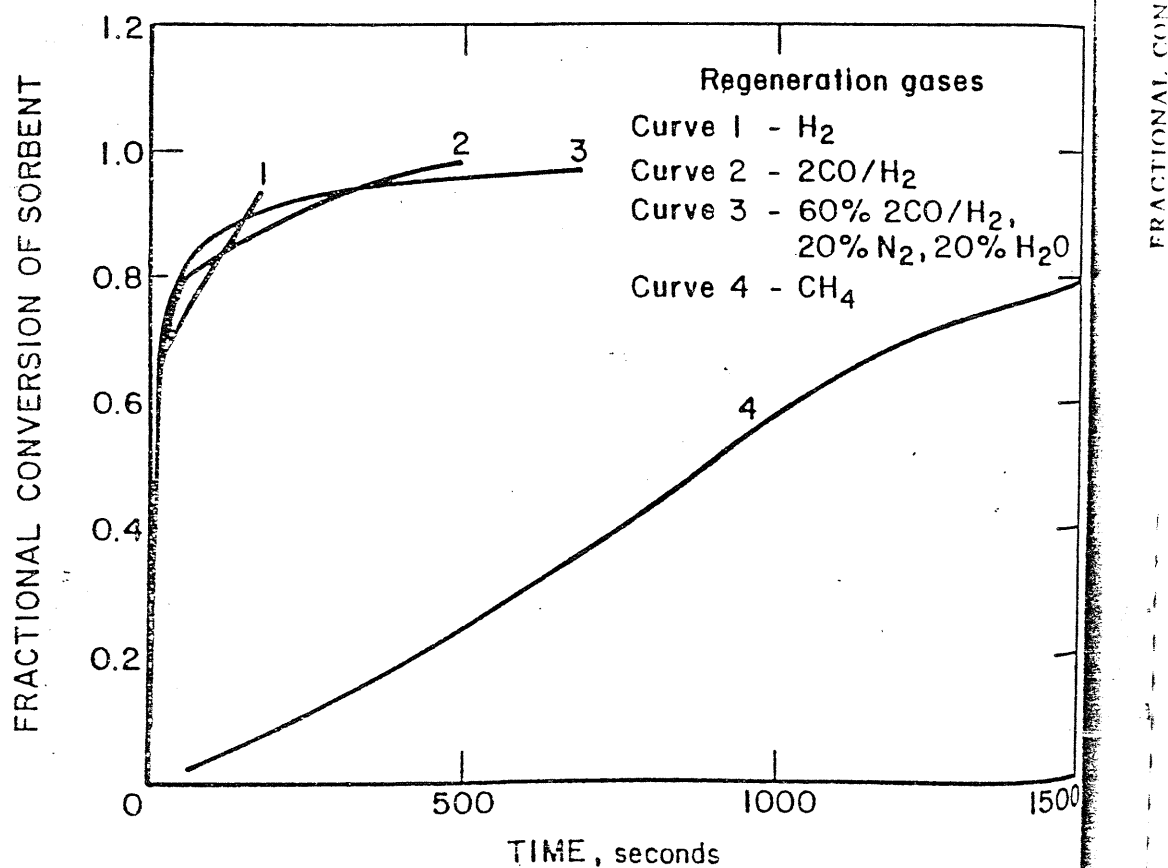


FIGURE 3. REGENERATION OF CuO WITH DIFFERENT GASES AT 400°C

gas-based reduction reaction is extremely sensitive to temperature; a temperature of at least 800°F is required to achieve a high sorbent fractional conversion (>95%) within an acceptable time limit (30 minutes). A comparison of the regeneration of sorbent with natural gas at 750°F (400°C) and 840°F (450°C) is shown in Figure 4.

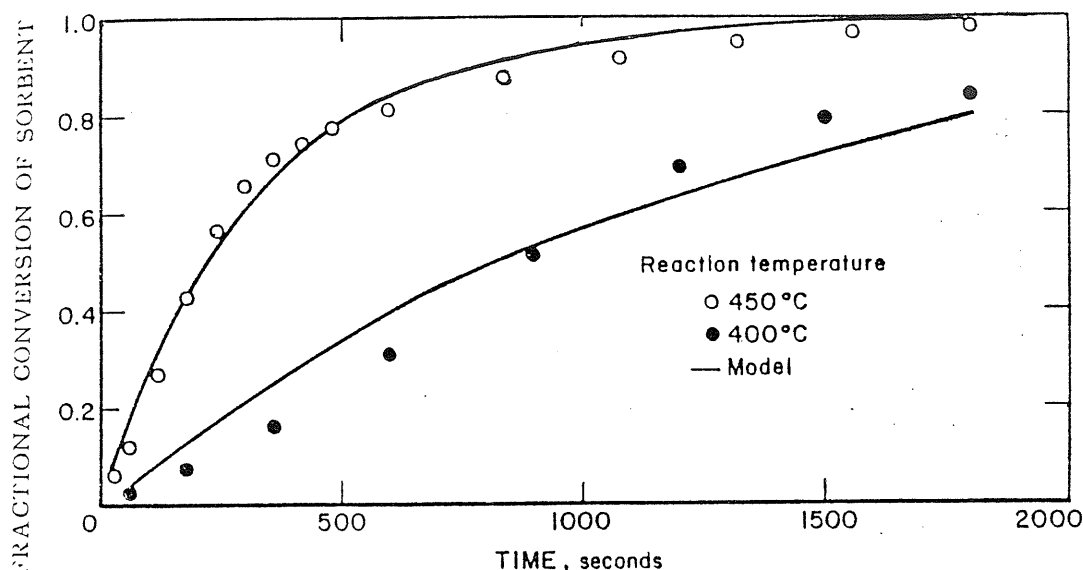


FIGURE 4. REGENERATION OF CuO WITH CH_4

PROCESS DESIGN CONSIDERATIONS

This section evaluates the technical considerations required to bridge the gap between process application and experimental results. The design and scale-up of a flue gas treatment process using the fluidized-bed copper oxide concept must be based on the functional relationships between process design parameters and the reaction rate phenomena established in the experimental evaluations. The key variables and operating parameters associated with the sorbent material, the fluidized-bed absorber, and the moving-bed regenerator, as well as their qualitative functional dependence on other system parameters, are listed in Table 1. No distinction was made between independent and dependent variables. Key components associated with the process design are discussed below, beginning with a general evaluation of the system layout.

Table 1. Identification of Key Operating Parameters for the Fluidized-Bed Copper Oxide Process

<u>SORBENT</u>	
<u>Design Parameter</u>	<u>Functional Dependence</u>
• Support Material	• effectiveness, attrition resistance, cost
• Copper Content	• effectiveness, attrition resistance, manufacturing limitations, cost
• Sphere Size	• effectiveness, attrition resistance, manufacturing limitations, gas entrainment, pressure drop
<u>FLUIDIZED-BED ABSORBER</u>	
<u>Design Parameter</u>	<u>Functional Dependence</u>
• Superficial Velocity	• bed cross-sectional area, flue gas volumetric flow rate
• Sorbent Mean Residence Time	• recirculation rate, bed height, crosssectional area
• Bed Height	• gas/sorbent residence time, pressure drop
• Temperature	• flue gas inlet temperature, internal heat generation
• NH ₃ Injection Rate	• NO _x reduction efficiency, NH ₃ emissions, bed height
<u>MOVING-BED REGENERATOR</u>	
<u>Design Parameter</u>	<u>Functional Dependence</u>
• Reactor Volume	• maximum sorbent recirculation rate, regeneration reaction kinetics
• Operating Temperature	• reducing gas type, reaction kinetics, degree of sorbent regeneration
• Reducing Gas Type	• required regenerator performance, cost
• Reducing Gas Flow Rate	• reducing gas type, reaction chemistry, degree of sorbent regeneration

System Layout and Operational Description

A simplified process flow diagram for the Fluidized-Bed Copper Oxide Process is shown in Figure 5. In power plant applications the fluidized-bed

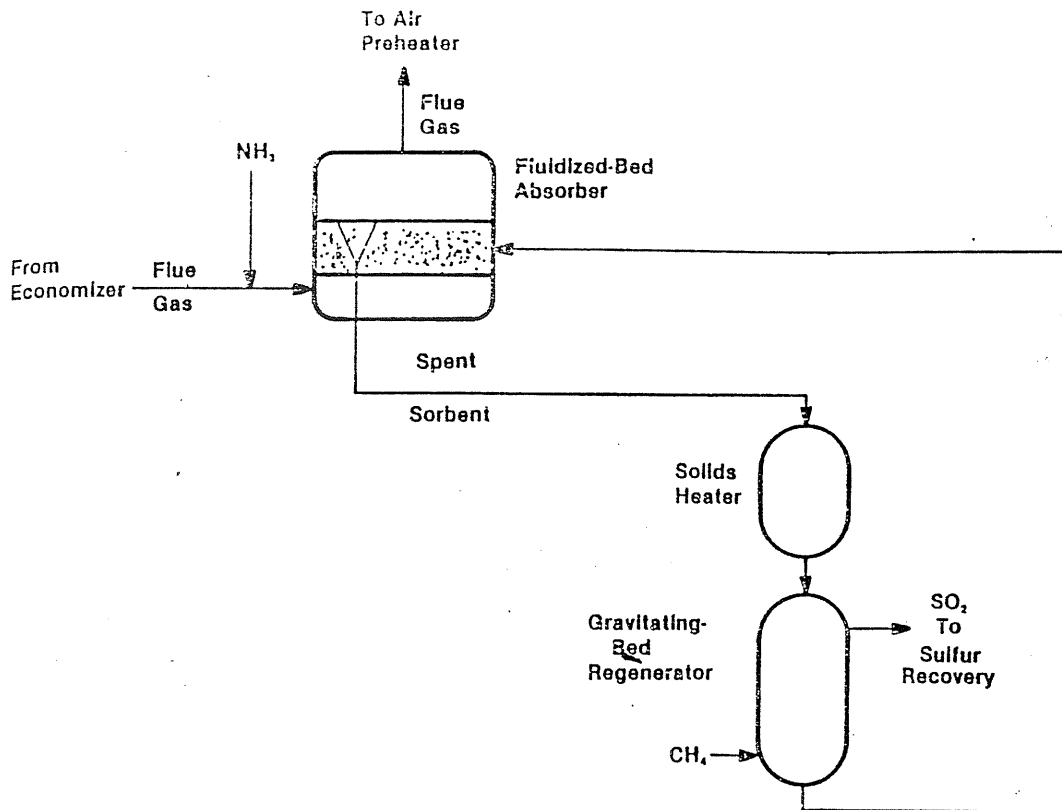


FIGURE 5. SIMPLIFIED FLUIDIZED-BED COPPER OXIDE
PROCESS FLOW SHEET

absorber(s) will be located between the plant economizer and air heater, where the flue gas temperature is typically above 650°F . Upstream of the absorber, ammonia is injected into the flue gas through a piping grid located within the flue gas ductwork. The sulfur dioxide and nitrogen oxides removal reactions occur in the absorber and, owing to the exothermic nature of these reactions, raise the exit temperature of the flue gas in proportion to the amount of sulfur dioxide and nitrogen oxides removed. The flue gas temperature at the exit of the absorber could be 50°F , or more, higher than the temperature at the absorber inlet for a high sulfur coal application. The treated flue gas is then ducted to the air preheater; since virtually all of the SO_2 has been removed from the flue gas (lowering the acid dew point), the air preheater can be designed for increased heat transfer. If required, the flue gas exiting the air preheater can be conditioned to maintain maximum electrostatic precipitator efficiency using tail gas from the by-product sulfur recovery system (a sulfuric

acid or elemental sulfur plant) to replace the traces of SO_2 removed in the process. Both the electrostatic precipitator and the induced-draft fans would be positioned in their normal location between the air preheater and the stack.

The sulfated sorbent continuously leaves the fluidized-bed absorber through overflow pipes and weirs, and is pneumatically transported with preheated air either to a solids heater or directly to the moving-bed regenerator. The need for a solids heater is dependent on the regeneration gas to be used. If hydrogen or a mixture of hydrogen and carbon monoxide is used for sorbent regeneration, the regeneration reactions are fast enough at the absorption temperature (approximately 750°F), and no solids heater is required. However, if natural gas is selected as the reducing gas, regeneration must take place at a temperature of at least 850°F to ensure a moderately fast reaction and a reasonably sized regeneration vessel. In the latter case, a solids heater is required to increase the sorbent temperature for regeneration.

If a solids heater is used, a separate gas-or oil-fired combustor will provide hot combustion gases for direct contact with the sorbent spheres. The heated sorbent will then flow by gravity into the regeneration vessel; valves will regulate the solids flow and seal the solids heater from the regenerator. In the regeneration vessel, the sulfated sorbent is regenerated by reaction with the reducing gas (CH_4 , H_2 , or a mixture of CO and H_2) flowing countercurrent to the sorbent (reactions 3 through 5). The regenerated sorbent leaves the regenerator at the bottom of the reactor. The sorbent is then pneumatically conveyed in heated air to the absorber. During solids transport, the copper formed during regeneration is oxidized to copper oxide (reaction 6).

The following raw materials are required by the process:

- copper-impregnated alumina sorbent to replace that lost through attrition
- reducing gas for sorbent regeneration (CH_4 , H_2 , or a mixture of CO and H_2)
- ammonia
- water for the by-product sulfur recovery conversion plant
- steam for ammonia vaporization.

Power is required for the induced-draft booster fan, solids transport blowers, solids heater combustor blower, and the by-product sulfur recovery conversion plant.

Fluidized-Bed Absorber

The fluidized-bed absorber is the most important component of the process. Its design establishes the sulfur dioxide and nitrogen oxides removal efficiencies, and primarily sets the design requirements for all of the other major system components. Because of the large volumes of flue gas that must be handled by the absorbers (one 500-MWe unit will generate approximately 1.2×10^6 scfm of flue gas), its physical design must be simple—a refractory-lined steel “box” that relies entirely on the transport-disengaging height (TDH) above the expanded bed to return sorbent spheres to the bed, and an appropriate “bubble cap” flue gas distributor plate that provides adequate mixing of the sorbent spheres. A pictorial representation of one possible absorber design is shown in Figure 6.

Before discussing the parametric relationships that affect the absorber’s sulfur dioxide and nitrogen oxides removal capabilities, it is important to

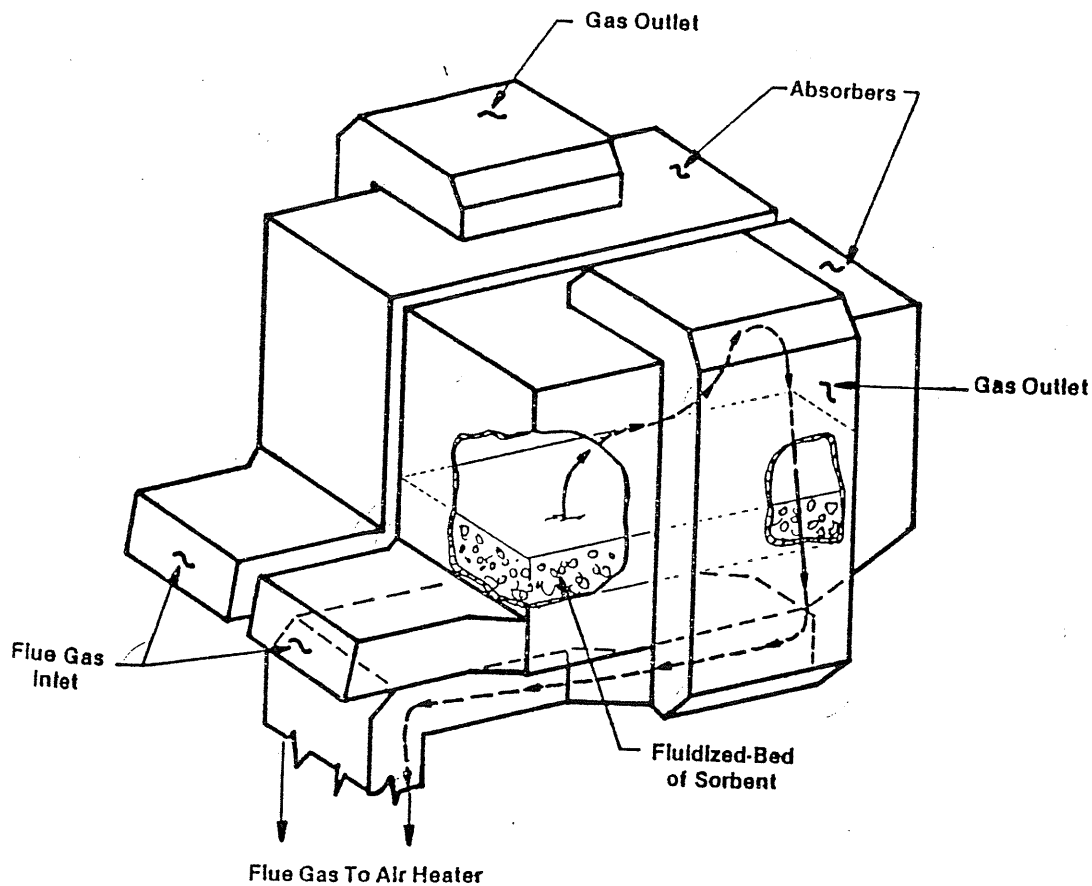


FIGURE 6. ABSORBER DESIGN CONFIGURATION

establish practical design limitations. For both economic and operational reasons, it is highly desirable to minimize the size and number of operating absorbers. The overall volume of the absorber is primarily determined by the cross-sectional area of the bed and the total height required for the expanded bed and the transport-disengaging height. The cross-sectional area required decreases as the bed superficial gas velocity increases. However, the practical limitations of excessive pressure drop, bubble cap erosion (by fly ash), excessive sorbent attrition (by jet impingement), and high transport-disengaging height will limit the superficial gas velocity to a value less than 5 ft/sec. The expanded-bed height is limited by the maximum tolerable absorber pressure drop based on its effect on the cost of moving the flue gas and its impact on boiler construction. An expanded-bed height ranging between 3 and 4 feet, combined with a bed superficial gas velocity of 4 ft/sec, should yield an overall absorber pressure drop of approximately 20 inches of water. This flue gas pressure drop should be acceptable from an economic and operational perspective. With these design considerations in mind, the parametric relationships that determine the absorber emissions-control performance will be reviewed.

The removal of sulfur dioxide by the copper-impregnated spheres is dependent on the average amount of unreacted copper that is in contact with the flue gas in the fluidized-bed absorber. This is controlled by the initial copper content of the sorbent, the pore structure of the support, and by the mean residence time of the sorbent in the bed. The initial copper content of the sorbent is a function of the sorbent manufacturing process and regeneration. The mean sorbent residence time is controlled by the sorbent recirculation rate and the height of the expanded bed for a specific cross-sectional area. The copper utilization obtained (moles of SO_2 removed for each mole of available copper) is also dependent on the mean sorbent residence time in the bed.

The relationship between the mean sorbent residence time in the absorber and sulfur dioxide removal, as established in previous tests using a 40-inch by 48-inch fluidized-bed absorber for data taken at a constant volumetric flue gas flow, is shown in Figure 7.⁶ It can be seen that for a specific expanded-bed height, the shorter the mean sorbent residence time, the greater the sulfur dioxide removal efficiency. Alternatively, for a specific mean residence time, larger bed heights increase sulfur dioxide removal efficiency. This clearly confirms that sulfur dioxide removal efficiency increases as the mass of available copper in contact with the sulfur dioxide laden flue gas increases. Assuming

that the absorber volume is established by the practical design considerations discussed previously, only the sorbent recirculation rate can be varied to control the mean sorbent residence time in the absorber. The sorbent recirculation rate is, therefore, an important parameter in the optimization of the process.

The effect of the sorbent recirculation rate on sulfur dioxide removal efficiency is shown in Figure 8.⁶ As would be expected, sulfur dioxide removal efficiency increases with increasing sorbent recirculation rate for specific values of expanded-bed height and unreacted copper. This occurs because increasing the sorbent recirculation rate decreases the mean sorbent residence time, which places more unreacted copper in contact with the flue gas. However, there are practical design considerations associated with increasing the sorbent recirculation rate:

- The amount of sorbent that must be heated (and consequently the energy required) is directly proportional to the sorbent recirculation rate.

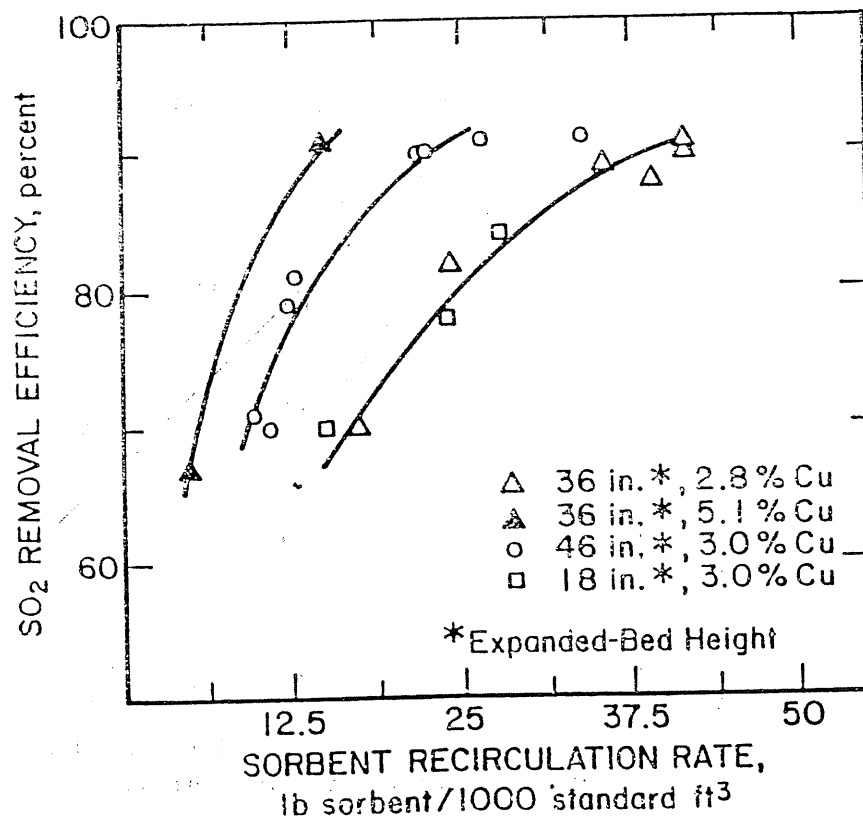


FIGURE 8. SORBENT RECIRCULATION RATES REQUIRED FOR SULFUR DIOXIDE REMOVAL

- Sorbent attrition losses increase with increasing sorbent recirculation rate.
- The size of the pneumatic transport equipment, solids heater, and sorbent regenerator increase with increasing sorbent recirculation rate.
- Copper utilization decreases with increasing sorbent recirculation rate.

Data from the 40-inch by 48-inch fluidized-bed and microbalance reactor tests are used in Figure 9 to show how the sorbent recirculation rate affects copper utilization.⁶ These data show that copper utilization decreases as the sorbent recirculation rate increases. Since the chemical reactions occurring in the regenerator do not selectively reduce copper sulfate, decreasing the copper

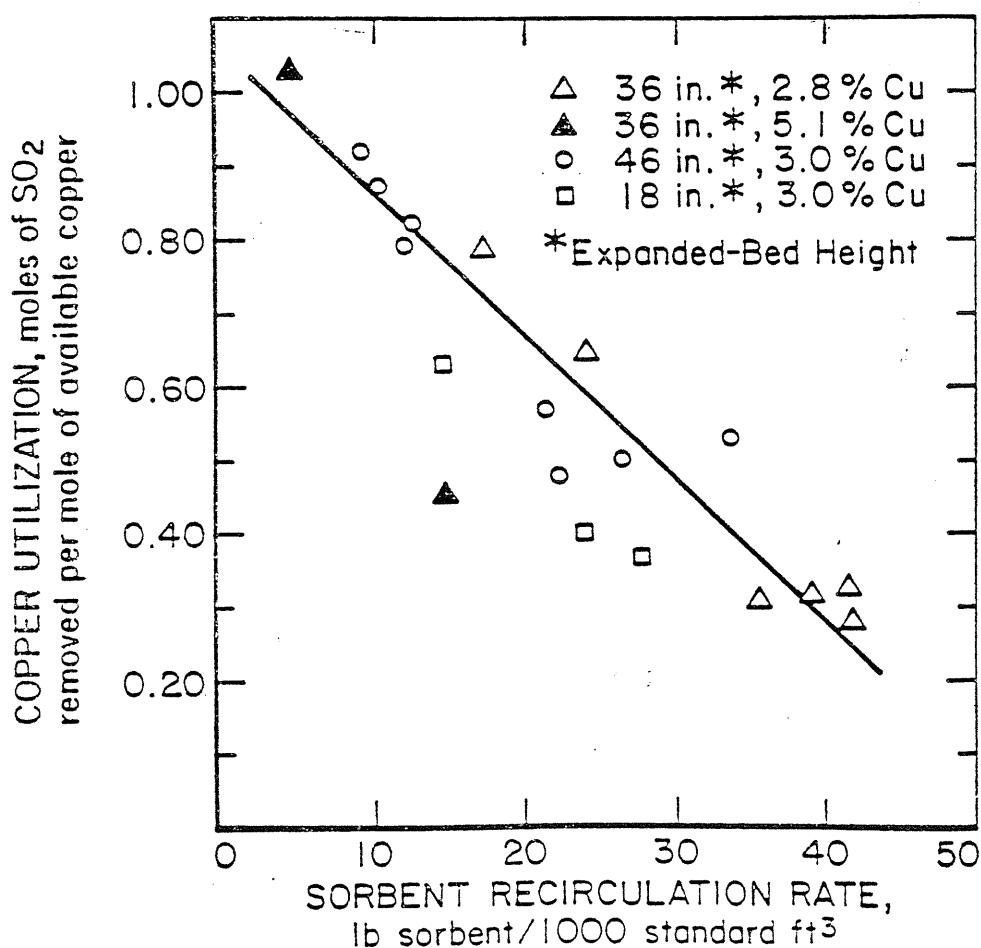


FIGURE 9. EFFECT OF SORBENT RECIRCULATION RATE OF COPPER UTILIZATION

utilization results in a waste of energy and reducing gas because at lower copper utilizations, more unreacted copper oxide will be reduced to copper per mole of sulfur dioxide removed. Therefore, once the bed volume is established for the design, optimization of the process will depend on minimizing the sorbent recirculation rate (maximizing the mean sorbent residence time) while maintaining the desired sulfur dioxide removal efficiency.

Obtaining the minimum practical sorbent recirculation rate is best achieved by increasing the initial copper content of the sorbent to the highest practical level (without increasing sorbent attrition) and increasing the extent of the sorbent regeneration reaction. Absorber modeling with data from micro balance reactor tests for three concentrations of copper supported on alumina was performed by the Pittsburgh Energy Technology Center and was reported by Ratafia-Brown et al.⁷ The model shows the following impact on sorbent recirculated rates:

- Increasing the sorbent copper content from 5.6 percent to 7 percent decreases the required sorbent recirculation rate by 15 percent.
- Increasing the sorbent copper content from 5.6 percent to 11 percent decreases the required sorbent recirculation rate by 40%.

Economic evaluations have shown that optimization of the sorbent recirculation rate will significantly reduce process capital costs and, to a lesser degree, reduce the operating costs associated with the Fluidized-Bed Copper Oxide process?

The removal of nitrogen oxides from the flue gas stream in the fluidized-bed absorber must also be considered in a technical evaluation of the process. The sorbent in this case is a catalyst for the reduction of nitrogen oxides in the presence of ammonia. As long as there is sufficient copper sulfate present in the fluidized bed to catalyze the reaction, the nitrogen oxides removal efficiency will be independent of that obtained for sulfur dioxide. The nitrogen oxides removal efficiency will depend on the amount of ammonia added to the flue gas to complete the reaction. Currently, there are insufficient data available to determine whether the sorbent recirculation rate or the mean sorbent residence time affects the amount of ammonia required to achieve a desired nitrogen oxides removal efficiency. However, results from tests conducted in the 40-inch by 48-inch fluidized-bed absorber at constant volumetric flue gas flow and sorbent recirculation rate identify a dependence on the expanded-bed

height in the absorber. The relationship between the expanded-bed height in the absorber and the ammonia-to-nitrogen oxides (NH_3/NO_x) molar ratio required to achieve 90 percent removal of nitrogen oxides is shown in Figure 10.⁶ This suggests that the amount of ammonia that must be added to the flue gas to achieve a desired nitrogen oxides removal efficiency decreases with increasing expanded-bed height. Therefore, the expanded-bed height is an important parameter in optimization of both sulfur dioxide and nitrogen oxides removal.

Solids Heater

If methane is selected as the reducing agent for sorbent regeneration, a heater will be required to raise the solids to a temperature that allows the

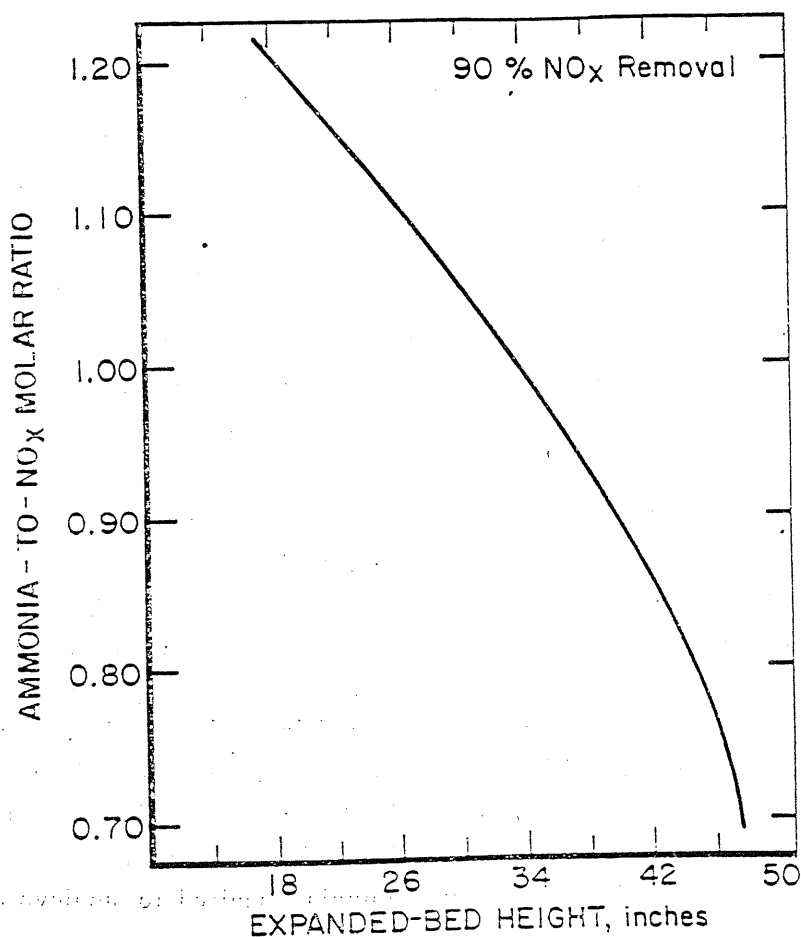


FIGURE 10. AMMONIA REQUIREMENTS FOR NO_x REMOVAL AT DIFFERENT BED HEIGHTS

regeneration reaction to be completed within the residence time of the regeneration reactor. This temperature is likely to be between 850°F and 950°F. The proposed design for the solids heater is a fluidized bed having several stages to increase thermal efficiency and reduce its size. It could be constructed of carbon steel with a refractory lining.

A schematic of the proposed solids heater design³ is shown in Figure 11. A separate gas-or oil-fired combustor will be used to provide hot combustion gas for the heater; the blower shown in the schematic will also be used to provide the air required to fluidize the sorbent pellets in the solids heater. The combustion gas will be split into two streams to ensure that the gas entering each stage is approximately 1200°F. (This temperature limit is selected to prevent sintering of the sorbent spheres.) This design approach results in a calculated thermal efficiency of approximately 50 percent compared to a thermal efficiency of about 35 percent for a single-stage design. The hot gas leaving the solids heater can be combined with flue gas exiting the fluidized-bed absorber to recover additional sensible heat in the plant air preheater.

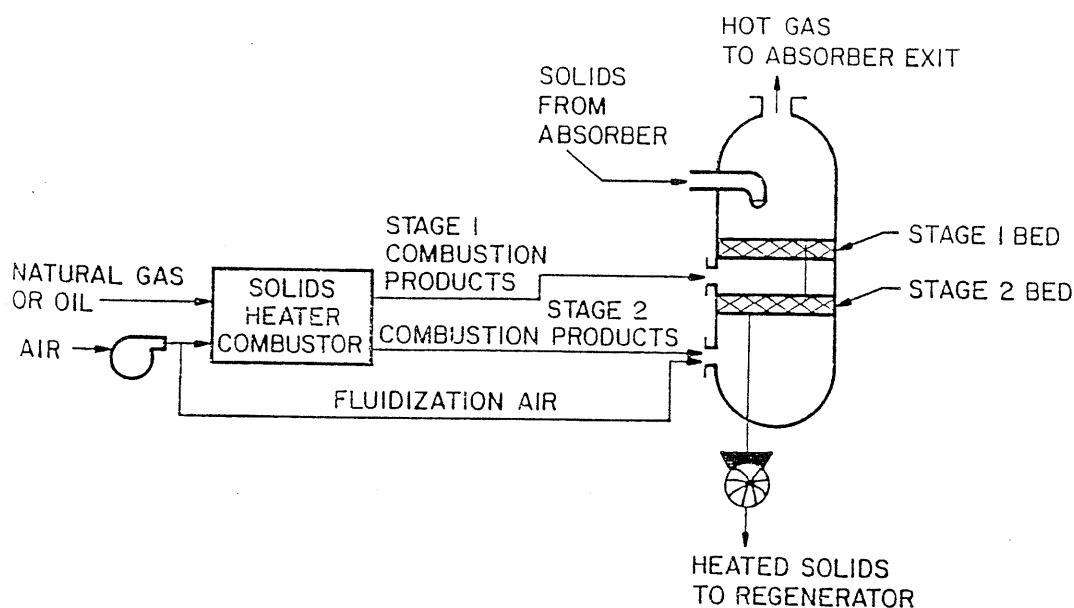


FIGURE 11. SCHEMATIC OF SOLIDS HEATER

Regenerator

The regenerator can be designed for either batch or continuous mode operation. However, to minimize the number of vessels and the vessel size, as

well as simplify regenerator operation, continuous operation is proposed. The regenerator is designed as a countercurrent, moving-bed reactor in which the sorbent spheres move down through the vessel by gravity, while the reducing gas is injected at the reactor base and rises upward through the bed. Based on a power plant application using 3.5 percent sulfur coal, 90 percent sulfur dioxide removal, natural gas as the reductant, and 99.5 percent conversion of copper sulfate to copper, the regenerator off-gas has the following composition:

- SO_2 — 33 percent
- CO_2 — 22 percent
- H_2O — 44 percent
- CH_4 — 1 percent

The regenerator off-gas is conveyed to a by-product sulfur recovery plant, producing either sulfuric acid or elemental sulfur. Note that the water generation exceeds SO_2 production owing to simultaneous reduction of unreacted copper oxide in the regenerator.

The regenerator vessel could be constructed of carbon steel with a refractory lining. Regenerated sorbent would exit the bottom of the regenerator by gravity, flowing through hoppers with the solids flow controlled by a variable-opening gate valve located at each hopper outlet.

A computer model of the regenerator reactor was created to establish regenerator performance with natural gas as the reducing gas.⁹ The plug flow reactor model used in the ASPEN process simulator served as a basis for the model. This is a rigorous model that is capable of simulating the operation of a tubular reactor when the reactor stoichiometry and kinetics are known and when all of the reactor substreams are assumed to be in plugflow (no axial diffusion of mass or axial conduction of energy). The reaction stoichiometry used in the model corresponds to that given in Equations 3 through 5, with an additional equation describing the reduction of unreacted copper oxide to copper. The regeneration reaction kinetics subroutine added to the ASPEN plug-flow model is based on the results of microbalance tests⁴ and assumes first-order reactions with respect to the reducing gas concentration and the unreacted copper sulfate and copper oxide. Because of the apparently strong temperature dependence of the reduction reaction, the Arrhenius equation is used to correlate reaction rate with temperature.

The modeling results indicate that a sorbent regenerator efficiency exceeding 99 percent is possible; for the particular design application studied an inlet solids temperature of approximately 930°F, and a reactor residence time of 32.5 minutes yields a CuSO_4 and CuO conversion of 99.3 percent and a methane conversion of 94 percent. Because the overall controlling chemical reactions are endothermic for high loadings of sulfur on the sorbent, the solids temperature will drop as much as 34°F for conditions resulting in a 99 percent sorbent conversion.

While the sorbent conversion efficiency is of primary concern because of the benefits derived from reducing the sorbent recirculation rate to the fluidized-bed absorbers, the concentration of combustible gases (CH_4 , CO , or H_2) in the regenerator off-gas is also critical and should be minimized. In the case where the gas is fed to a sulfuric acid plant, the sulfur dioxide concentration used for the plant design basis must be reduced if combustible gases are present to allow for the heat of combustion of these gases in the acid plant converter system. This requires the processing of a greater gas volume per ton of acid produced, increasing operating costs and plant capital costs because of the larger equipment required. In addition, the combustible gas levels leaving the regenerator must be monitored and controlled for safety reasons to ensure that concentrations do not exceed the lower explosive limit.¹⁰

Pneumatic Transport System

Operation of the Fluidized-Bed Copper Oxide flue gas treatment process for high sulfur dioxide removal necessitates the circulation of large quantities of hot sorbent between the absorber and the regenerator. For example, a power plant application burning 3.5 percent sulfur coal, with 90 percent sulfur dioxide removal, 5.5 percent copper content on the sorbent, and a 3-foot expanded-bed height in the absorber will require a sorbent recirculation rate exceeding 700,000 lb/hr. Pneumatic transport of such large quantities is likely to be the simplest, most cost-effective, and most reliable method of conveyance. Critical to the design of such a transport system is the minimization of sorbent attrition. The high cost of the sorbent (greater than \$2.50 per pound) demands minimal sorbent losses.

Two alternative transport system designs have been evaluated:

- A dilute-phase continuous-conveying system¹¹
- A dense-phase semicontinuous-conveying system⁷

The dilute-phase continuous system depends on the use of rotary valves to continuously feed the sorbent from a reactor vessel into a pneumatic transport line. The rotary valves simultaneously act as gas seals between areas of different pressure. Owing to the high-temperature environment seen in the process, these valves must be of high-alloy construction with watercooled bearings. As a result, their cost is high. Previous experience with this type of valve for sorbent feed rate control in the 40-inch by 48-inch fluidized bed has been disappointing, with high rates of physical attrition of the sorbent being observed.⁵ At high sorbent feed rates, the rotary valve feeder apparently grinds the sorbent. In addition, feeder reliability is suspect in this operating environment.

The dense-phase, semicontinuous transport system eliminates the need for rotary valves by using blow tanks; blow tanks are ideal for conveying free-flowing or fluidizable material that is friable or abrasive. A pictorial representation of a dense-phase transport system is given in Figure 12. Sorbent exits the reactor vessel (absorber or regenerator) and is fed by gravity into a large surge hopper. Sorbent flow rate through the absorber and regenerator is controlled by the sorbent recirculation rate maintained by variable-opening gate valves at the exit of the regenerator. The surge hopper provides a short-duration storage area for the sorbent and permits continuous flow through the reactors, while solids transport by the blow tanks is semicontinuous. The solids in the surge tank flow (by gravity) into multiple blow tanks that discharge alternately into a single conveying line; as one tank is discharging, the second tank is filling. Each conveying line receives transport air from a blower. To uniformly distribute the sorbent to all sections of the absorber, the large solids transport line, conveying solids from the regenerator to the absorber, will split into approximately eight smaller lines.

By-Product Sulfur Recovery System

Application of the Fluidized-Bed Copper Oxide process for power plant sulfur dioxide emissions control necessitates a parallel facility for treating the concentrated stream of sulfur dioxide produced in the regenerator. Two options are available for the treatment of this stream: a sulfuric acid plant or an elemental sulfur plant. Sulfuric acid plants are commercially available, and there would be little problem in integrating a commercial design with this flue gas treatment process.

There are two promising methods that have been evaluated for reducing concentrated streams of sulfur dioxide to produce elemental sulfur:

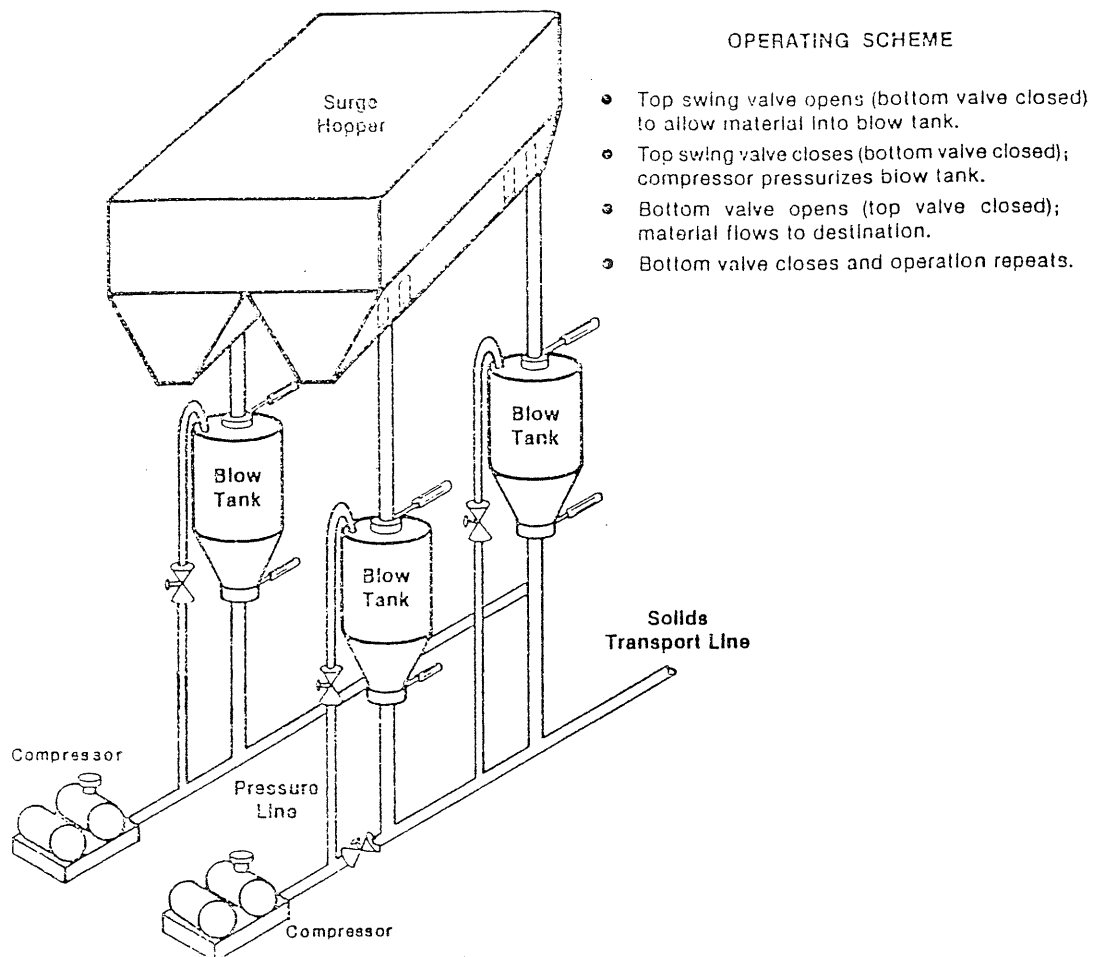


FIGURE 12. PROPOSED DESIGN FOR A DENSE-PHASE PNEUMATIC, TRANSPORT SYSTEM

- The Foster Wheeler RESOX Process
- The Allied Chemical Sulfur Dioxide Reduction Process

The EPRI-sponsored pilot-scale (1-MW) and prototype-scale (42-MW) development units have shown the RESOX process to be a technically viable and relatively flexible method for reducing sulfur dioxide to elemental sulfur using coal as the reductant. In this process, the sulfur dioxide rich gas is passed through a vessel containing crushed coal; here, the sulfur dioxide is reduced to gaseous elemental sulfur, and the liberated oxygen combines with a portion of the coal to form carbon dioxide. An elemental sulfur yield of 70-80 percent can be expected with this process.

The Allied Chemical process is commercially operated, but it has not been applied widely. The first application of this technology to flue gas desulfurization for electric utilities was undertaken at Northern Indiana Public Service Company's Dean H. Mitchell station in Gary, Indiana. The process consists of two major operating sections. In the primary reduction section, methane is combined and reacted with the gas being treated to directly produce sulfur, carbon dioxide, water, and hydrogen sulfide. More than half of the sulfur dioxide entering the reactor is converted to elemental sulfur in this stage. The second operating section involves a double Claus conversion with intermediate and final sulfur condensation. A total elemental sulfur yield of at least 95 percent is expected with this process.

A comparative economic evaluation of the available by-product sulfur recovery processes (a sulfuric acid plant, the Resox Process, and the Allied Chemical Process) did not clearly identify the most advantageous for electric utility application.¹² Therefore, the choice between these processes would depend on marketability of the by-product (sulfur vs. sulfuric acid) and process reliability. While it would appear that sulfur would be the most desirable by-product for most areas of the country, it can be concluded that a sulfuric acid plant clearly represents the most mature of the by-product sulfur recovery technologies.

ECONOMIC EVALUATION OF THE FLUIDIZED-BED COPPER OXIDE PROCESS

The process design and economics associated with the Fluidized-Bed Copper Oxide Process were extensively evaluated by the Science Management Corporation (SMC) between November, 1981, and May, 1983. Seven reports were completed during this time period, each covering a different technical and economic aspect of the process.⁷⁻¹³ The economic evaluation presented here for a new 500-MWe power plant application is based on the results of these previous studies updated to reflect current process operating and design data.

The power plant application for this process is based on a new, 500-MWe, coal-fired boiler, with an assumed Midwestern location, using the high-sulfur, East-Central U. S. coal documented in the EPRI Technical Assessment Guide.¹⁴ The power plant is identical to that described in the EPRI report "Economic Evaluation of FGD Systems."¹⁵ The fuel is Illinois No. 6 bituminous coal having

a heating value of 10,100 Btu/lb and containing 4 percent sulfur and 16 percent ash (on an as-fired basis).

The Fluidized-Bed Copper Oxide Process treats the flue gas at the exit of the economizer, since the temperature desired for the absorption reaction is close to the economizer exit temperature. The flue gas composition used in this evaluation is presented in Table 2 and was estimated based on the assumption that 95 percent of the sulfur in the coal is emitted in the flue gas as sulfur oxides, with 99 percent as SO_2 and 1 percent as SO_3 .

Table 2. Flue Gas Composition and Flow Rate at Economizer Outlet Used in the Economic Evaluation of the Fluidized-Bed Copper Oxide Process

Component	Concentration	Flow Rate	
		lb-mole/hr	lb/hr
CO_2	13.75%	23,704	1,043,000
SO_2	3,368.6 ppm	581	37,168
SO_3	34.0 ppm	5.86	469
HCl	78.6 ppm	13.55	494
O_2	3.22%	5,557	177,828
N_2	73.34%	126,644	3,546,043
H_2O	9.15%	15,781	284,060
NO	643.0 ppm	111	3,326
NO_2	4.3 ppm	0.74	34
		172,378	5,092,422

Economizer Outlet Temperature=374°C (705°F)

Basis: 522-MWe, new, coal-fired power plant, burning the 4 percent sulfur

East-Central U. S. coal documented in the EPRI Technical Assessment Guide.¹⁴

The process conceptual design is based on a removal efficiency of 90 percent for both nitrogen oxides and sulfur dioxide emissions. This level of emissions reduction is equal to that required by the 1979 New Source Performance Standards (NSPS) for sulfur dioxide but exceeds the NSPS levels for nitrogen oxides.

The system design characteristics used as a basis for the economic evaluation of the Fluidized-Bed Copper Oxide Process are described in Table 3. For this application, four operating trains and one spare process train are used.

**Table 3. System Characteristics Selected for the Evaluation
of the Fluidized-Bed Copper Oxide Process**

System Characteristics	Option Selected
• SO ₂ /NO _x Sorbent Reactors	Fluidized Bed
• Sorbent Heater	Two-Stage Fluidized-Bed Solids Heater
• Source of Hot Gas Required for Solids Heating	Methane Combustion
• Sorbent Regenerator Reactor	Counter-Current Gravitating Bed
• Reducing Gas Used	Methane (other gases have been tested and could also be used)
• By-Product Sulfur Recovery	The concentrated SO ₂ stream produced in the regenerator reactor is sent to a contact sulfuric acid plant (elemental sulfur could be produced instead of sulfuric acid if desired)
• Solids Transport System	A semicontinuous, dense-phase solids transport system using surge hoppers and blow tanks

**Table 4. Absorber Design Parameters Used in the Economic
Evaluation of the Fluidized-Bed Copper Oxide Process**

Parameter	Design Value
SO ₂ Removal Efficiency, percent	90
NO _x Removal Efficiency, percent	90
Inlet SO ₂ Concentration, ppm (volume)	3,368
Inlet NO _x Concentration, ppm (volume)	643
Absorber Bed Temperature, °F	780
Sorbent Recirculation Rate (total), lb/hr	1,266,679
Sorbent Recirculation Rate, lb Sorbent/1000 Standard ft ³ Flue Gas	17.43
Available Cu, percent	6.62
Cu/S Mole Ratio	2.25
Copper utilization, Mole SO ₂ Removed per Mole Available Cu	0.4
NH ₃ /NO _x Mole Ratio	1.0
Bed Superficial Gas Velocity, ft/sec	4.2
Expanded-Bed Height (fluidized), ft	3
Bed Pressure Drop, inches water	18
Transport-Disengaging Height, ft	25
Sorbent Attrition, percent of the bed inventory per hour	0.08

Basis: 522-MWe, new, coal-fired power plant, 4 percent sulfur coal, 7.44 lb SO₂/MBtu and 643 ppm NO_x flue gas emissions, with process achieving 90 percent SO₂ removal and 90 percent NO_x removal.

Each process train consists of a fluidized-bed absorber, a solids heater, a regenerator, and solids transport equipment. The values used for specific operating parameters in the fluidized-bed absorber are based on test results reported by Yeh et al.⁵ These operating parameters are described in Table 4. Based on these design requirements, a material and energy balance were

Table 5. Fluidized-Bed Copper Oxide Process Energy Requirements for a 500-MWe Power Plant Application (Including Sulfuric Acid Plant)

<u>Energy Type</u>	<u>Energy Required¹</u>	<u>Energy Requirements Converted to Electricity Output,² kW</u>	<u>Percent of Boiler Output</u>
Electricity ³	10,067 kW	10,067	1.93
Steam ⁴	1.303×10^6 Btu/hr	155	0.03
Natural Gas ⁵	312.103×10^6 Btu/hr	32,630	6.25
Heat Credit ⁶	67.6×10^6 Btu/hr	(7,067)	(1.35)
		35,785	6.86

Notes:

- ¹ Calculated energy requirement for the Fluidized-Bed Copper Oxide Process (including sulfuric acid plant).
- ² Each energy form has been calculated on the basis of electricity output from the power plant. For steam, a thermal efficiency of 88 percent was used to determine the energy input required to generate one Btu of steam energy; then the energy requirement was converted to electricity output at the plant heat rate. Both the heat-credit and methane were assumed to replace heat input to the boiler on a one-to-one basis and then converted to electricity output at 9,569 Btu/kWh.
- ³ Includes induce-draft fans, solids transport air blowers, combustor/solids heater blower, and acid plant.
- ⁴ Based on a datum of saturated water at 32°F.
- ⁵ Based on a heating value of 21,502 Btu/lb. Includes methane for solids heating and regeneration.
- ⁶ Based on added process energy recovered in the air heater and returned to the boiler.

Basis: 522-MWe, new, coal-fired plant; 4 percent sulfur coal; 7.44 lb SO₂/MBtu and 643 ppm NO_x flue gas emissions, with process achieving 90 percent SO₂ removal and 90 percent NO_x removal. Upper midwest location represents project beginning January, 1983, ending December, 1985. Average cost basis, June, 1984. Four operating trains and one complete spare train included. Investment includes flue gas cleanup process ductwork but excludes stack plenum and stack.

Table 6. Fluidized-Bed Copper Oxide Process Raw Materials Requirements for a 500-MWe Power Plant Application (Including Sulfuric Acid Plant)

Raw Material	Quantity
Natural Gas ¹	14,515 lb/hr
Sorbent ²	772 lb/hr
Ammonia ³	1,913 lb/hr
Steam ⁴ (100 psig, sat.)	1,173 lb/hr
Process Water ⁵	196 gal/hr
Cooling Water ⁵	335×10 ³ gal/hr

Notes:

- ¹ Methane is used for solids heating and regeneration.
- ² Sorbent makeup requirements are based on a rate of attrition equal to 0.08 percent of the fluidized-bed inventory per hour.
- ³ Ammonia is used for the reduction of nitrogen oxides.
- ⁴ Steam is required for ammonia vaporization.
- ⁵ Process and cooling water are required for the acid plant.

Basis: 522-MWe, new, coal-fired power plant; 4 percent sulfur coal; 7.44 lb SO₂/MBtu and 643 ppm NO_x flue gas emissions, with process achieving 90 percent SO₂ removal and 90 percent NO_x removal.

calculated for the 500-MWe conceptual design in order to identify equipment requirements, raw material needs, and process energy requirements that provide a basis to estimate equipment capital costs, operating costs, and annual revenue requirements.

The energy requirements and raw material requirements for this process application are summarized in Tables 5 and 6. Sorbent makeup requirements are based on an assumed attrition rate of 0.08 percent of the bed inventory per hour. Steam is used in the process to vaporize ammonia.

In this economic evaluation of the integrated Fluidized-Bed Copper Oxide Process and sulfuric acid plant, capital cost estimates are based on major equipment costs developed from material and energy balances, and on factored costs for installation and ancillary equipment. Owing to the level of detail associated with this study-grade cost evaluation, the cost estimate is considered to be accurate to an overall variation of ±25 percent. The capital investment

and annual revenue requirements are given in dollars per kW and mills per kWh based on the net MWe rating. This net MWe rating is calculated by derating the 522-MWe output of the power plant by the energy consumption of the combined flue gas cleanup process and sulfuric acid plant. The capital investment estimate represents a project beginning in January, 1983, and ending in December, 1985. Costs are given in June, 1984, dollars.

The total plant capital investment is summarized in Table 7. A process contingency of 30 percent and a project contingency of 25 percent have been used for the flue gas cleanup process because only pilot-plant data are available and because the cost estimate is preliminary in nature. However, owing to the commercial availability of the acid plant, a 5 percent process contingency and 10 percent project contingency have been applied to it.

The first-year fixed and variable operating costs associated with the process are summarized in Table 8. The unit costs of raw materials and utilities used as a basis to determine the operating costs are documented in Table 9. Levelized capital charges of 4.76 mills/kWh were determined by taking 15.3 percent of the total capital requirement of 177.18 \$/kW (converted to mills/kWh). Combining this value with the first year operating costs (50.07 \$/kW-yr) converted to mills/kWh yields a first-year annual revenue requirement of 13.55 mills/kWh. A 30-year levelized annual revenue requirement of 25.10 mills/kWh (4.76 mills/kWh levelized capital charges plus 20.34 mills/kWh levelized operating costs) is obtained based on the assumption that a discount rate of 12.5 percent per year and an inflation rate of 8.5 percent per year apply to the operating costs over the life of the power plant. This corresponds to an annual cost of \$706 per ton of pollutants removed (sulfur dioxide and nitrogen oxides combined).

The largest cost factor associated with the annual revenue requirement is the makeup sorbent requirement. Minimizing sorbent attrition and sorbent cost is critical in the commercialization of the process. For example, if the sorbent cost is reduced to \$2.50/lb (which is not unrealistic), the levelized annual revenue requirement will drop to 16.8 mills/kWh, which is equivalent to an annual cost of \$472 per ton of sulfur dioxide and nitrogen oxides removed. Reducing the sorbent attrition by 50 percent would have a similar effect on reducing levelized annual cost. Additional cost savings can result from process optimization. An optimization study performed for a similar power plant application of the Fluidized-Bed Copper Oxide Process indicates that levelized

Table 7. Summary of Total Plant Capital Investment: Fluidized-Bed
Copper Oxide Process (Cost-Year: June, 1984)

	Capital Investment \$/kW	Percent of Total Direct Investment
<u>Direct Investment</u>		
NH ₃ Storage and Injection	1.77	2.20
Reactor Section (excluding catalyst)	21.12	26.22
Flue Gas Handling	11.22	13.93
Solids Heating	8.04	9.98
Regeneration	3.31	4.11
Solids Transport System	10.42	12.94
Sulfuric Acid Plant	<u>20.12</u>	<u>24.97</u>
Total Process Capital	76.01	94.34
General Facilities	<u>4.56</u>	<u>5.66</u>
Total Direct Investment	80.57	100.00
<u>Indirect Investment</u>		
Engineering, Design, and Supervision	5.64	7.0
A&E Contractor	1.41	1.80
Construction Expense	10.68	13.30
Contractor Fees	3.16	3.90
Process and Project Contingency	<u>47.16</u>	<u>58.50</u>
Total Indirect Investment	<u>68.04</u>	<u>84.45</u>
Total Plant Investment	148.61	184.45
<u>Other Capital Charges</u>		
Interest During Construction	17.83	
Prepaid Royalties	0.38	
Preproduction Costs	6.83	
Inventory Capital	6.83	
Initial Chemicals and Catalyst Charge	14.45	
Land	<u>0.05</u>	
Total Other Capital Charges	<u>28.57</u>	<u>35.46</u>
Total Capital Requirement	177.18	219.91

Basis: 522-MWe, new, coal-fired power plant; 4 percent sulfur coal; 7.44 lb SO₂/MBtu and 643 ppm NO_x flue gas emissions, with process achieving 90 percent SO₂ removal and 90 percent NO_x removal. Upper midwest location represents project beginning January, 1983, ending December, 1985. Average cost basis, June, 1984. Four operating trains and one complete spare train included. Investment includes flue gas cleanup process ductwork but excludes stack plenum and stack.

Table 8. Summary of Process Operating Costs:
Fluidized-Bed Copper Oxide Process
(Cost-Year: June, 1984)

	Annual Requirement	First-Year Operating Costs \$/kW-yr	Levelized Revenue Requirements Mills/kWh
<u>Fixed Operating Costs</u>			
Operating Labor	26,280	0.83	0.34
	staff-hours		
Maintenance Labor		1.29	0.52
Maintenance Material		1.93	0.78
Administration and Support Labor		0.63	0.26
Total Fixed Operating Costs		4.68	1.90
<u>Variable Operating Costs</u>			
Absorbent	4,139,538 lb	39.88	16.21
NH ₃	5,447 tons	1.99	0.81
Natural Gas	1,959,981 × 10 ³	14.92	6.06
	standard ft ³		
Acid Plant Catalyst		0.02	0.01
Steam	6,679 × 10 ³ lb	0.05	0.02
Power	5.7323 × 10 ⁷ kWh	6.63	2.69
Process Water	1,030 × 10 ³ gal	0.00	0.00
Cooling Water	1,907,489 × 10 ³ gal	0.74	0.30
Waste Product Disposal	0	0.00	0.00
Sulfuric Acid Sales	147,247 tons	-14.19	-5.77
Power Credit	4.0237 × 10 ⁷ kWh	-4.65	-1.89
Total Variable Operating Costs		45.39	18.44
Total Operating Costs		50.07	20.34

Basis: 522-MWe, new, coal-fired power plant; 519,006 kW net power generation; 5,695 hours of operation per year; 4 percent sulfur coal; 7.44 lb SO₂/MBtu and 643 ppm NO_x flue gas emissions, with process achieving 90 percent SO₂ removal and 90 percent NO_x removal. Upper midwest location represents project beginning January, 1983, ending December, 1985. Average cost basis, June, 1984. Plant life assumed to be 30 years. Levelization factor (2.314) based on inflation rate of 8.5% per year and a discount rate of 12.5% per year. Four operating trains and one complete spare train included. Investment includes flue gas cleanup process ductwork but excludes stack plenum and stack.

revenue requirements can be reduced 6 percent to 7 percent by increasing the sorbent copper content to 11 percent (by weight)⁷; the increased copper content permits a reduction of the sorbent circulation rate by approximately 4 percent, which yields reductions in capital and operating costs.

Table 9. Unit Cost of Raw Materials and Utilities Used in the Economic Evaluation

	Unit Cost
Copper Oxide Sorbent	\$5/lb
Natural Gas	\$3.95/MSCF
Power	\$0.06/kWh
Ammonia	\$190/ton
Steam	\$3.50/1,000 lb
Process Water	\$0.50/1,000 gal
Cooling Water	\$0.20/1,000 gal
Sulfuric Acid By-Product	\$50/ton

SUMMARY

The Fluidized-Bed Copper Oxide Process has been shown to be a simple and economic means of simultaneously removing sulfur dioxide and nitrogen oxides from the flue gas of coal-fired electric power generating facilities. The process produces no waste materials because the recovered sulfur is converted to a useful by-product, and the nitrogen oxides present in the flue gas are reduced to gaseous nitrogen and water.

An economic evaluation of the Fluidized-Bed Copper Oxide Process has found this process to be a promising alternative to limestone scrubbing. The total capital investment required for a 500-MWe coal-fired power plant application of the Fluidized-Bed Copper Oxide Process is 177.18 \$/kW (cost basis: June, 1984). The operating cost for this installation has been estimated to be \$706 per ton of flue gas contaminant removed (sulfur dioxide and nitrogen oxides combined).

To demonstrate the reliability and operability of the process, it must still be tested at a larger scale as an integrated process. Further optimization

process parameters is required during commercialization of the process.

Improvements to the Fluidized-Bed Copper Oxide Process that would reduce the sorbent attrition rate and the cost of the sorbent, and that would allow a reduction in the sorbent recirculation rate required to achieve desired emissions reductions could significantly reduce the capital and operating costs associated with the process.