For Pgh Coal Conference

ECONOMIC MODEL OF THE FLUIDIZED BED COPPER OXIDE PROCESS FOR SO_2/NO_x CONTROL

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ABSTRACT

The fluidized bed copper oxide process is an advanced concept for the simultaneous removal of SO_2 and NO_x from the flue gas of coal-fired power plants. Here, a systematic modeling framework is developed to evaluate the performance and cost of a conceptual commercial scale system. This paper focuses on economic evaluations of the process reflecting new performance and design assumptions. A key feature of the modeling framework is an ability to deal with process integration issues within the copper oxide process, with other parts of the pollution control system, and with the power plant. Sensitivity analyses of the model illustrate many of the key design and research issues for the copper oxide process.

INTRODUCTION

The fluidized bed copper oxide process is an advanced technology for controlling SO_2 and NO_x emissions from coal-fired power plants. The development of this process has been sponsored by the U.S. Department of Energy's Pittsburgh Energy Technology Center (DOE/PETC). Testing of the process began at PETC in 1975 and has progressed through several stages in three different test units [1-3]. The copper oxide process offers a number of potential advantages over more conventional approaches to SO_2 and NO_x control: (1) it combines SO_2 and NO_x removal in a single reactor vessel; (2) it is regenerative (i.e. the reagent is reused); and (3) it produces a saleable sulfur byproduct, in contrast to the sludge produced by conventional flue gas desulfurization (FGD) systems [4]. Conceptual designs of commercial scale copper oxide systems were developed in the early 1980's [5-7].

To evaluate the copper oxide process, a detailed performance and economic model was developed by Frey [8]. This model was implemented as part of a broader modeling framework, the Integrated Environmental Control Model (IECM) [9,10]. The IECM includes performance, emissions, and cost models for conventional and advanced technologies for pre-combustion, combustion, and post-combustion environmental controls. These component models can be configured to evaluate alternative environmental control strategies for coal-fired power plants. Details of the evolution of the IECM's copper oxide process and associated models (e.g., byproduct recovery) are described elsewhere [8,10,14,17].

The models characterize mass and energy balances for key process equipment. Capital, annual, and levelized costs are calculated using a standard approach [11]. The IECM has a unique capability to explicitly model uncertainties in the performance and cost of advanced technologies using Monte Carlo simulation. Previous versions of the copper oxide process model have been applied in a number of case studies to evaluate uncertainty in process costs, payoffs from process design improvements, the dependence of system cost on process design conditions and byproduct markets, and the likelihood that the advanced process will yield cost savings relative to conventional technology [8,12,13].

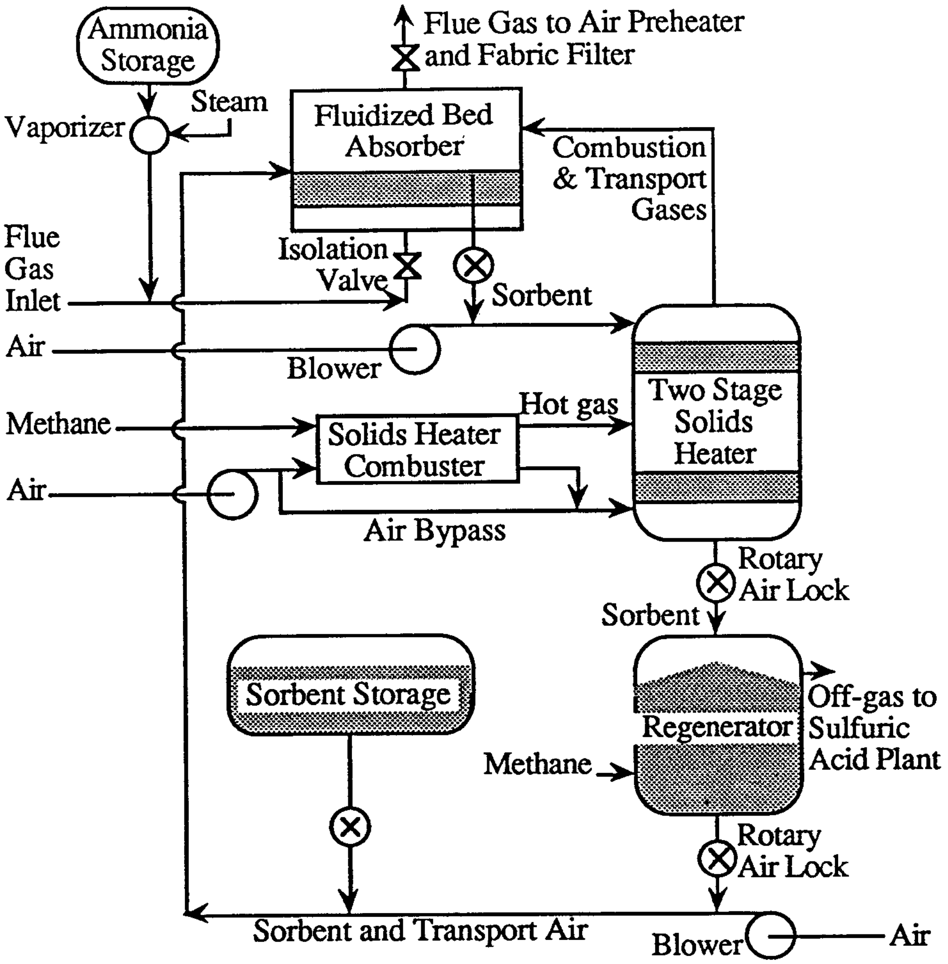

Figure 1. Schematic Diagram of the PETC Fluidized Bed Copper Oxide Process.

In a recent study [14], the performance model for the copper oxide process was updated to include new models for the kinetics of sulfation and regeneration, based on work by Harriott and Markussen [15] and Harriott [16]. The mass and energy balance for the sorbent were modified accordingly. The design basis for byproduct sulfur recovery and for calculating process energy requirements were also updated. The new performance model was applied to evaluate several design issues, including overall sulfur removal efficiency, fluidized bed absorber height, sorbent copper loading, and regeneration efficiency.

In this paper, the revised performance model is applied with the earlier economic model to make preliminary evaluations of key cost trade-offs, the dependence of system cost on process design conditions, and the implications of alternative process integration strategies between the copper oxide process and the elemental sulfur byproduct recovery system. As part of future work, the economic model will be revised based on efforts by A.E. Roberts and Associates, Inc. to complete a detailed cost estimate for a conceptual commercial plant.

PROCESS CHEMISTRY

The copper oxide process is shown in Figure 1. Small diameter (1/8 inch) copper-impregnated alumina spheres circulate between an absorber and regenerator. In the absorber, this sorbent is fluidized by the flue gas. The copper, as copper oxide, reacts with sulfur oxides. Ammonia injected into the flue gas reacts with nitrogen oxides, catalyzed by copper sulfate [4]. The energy released from these exothermic reactions can be recovered via the power plant air preheater. The net chemical reactions occurring in the absorber are:

$$CuO_{(s)} + SO_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow CuSO_{4\,(s)} \qquad (1)$$

$$CuO_{(s)} + SO_{3\,(g)} \rightarrow CuSO_{4\,(s)} \qquad (2)$$

$$4\ NO_{(g)} + 4\ NH_{3\,(g)} + O_{2\,(g)} \rightarrow 4\ N_{2\,(g)} + 6\ H_2O_{(g)} \qquad (3)$$

$$2\ NO_{2\,(g)} + 4\ NH_{3\,(g)} + O_{2\,(g)} \rightarrow 3\ N_{2\,(g)} + 6\ H_2O_{(g)} \qquad (4)$$

Sulfated sorbent is heated in a two-stage fluidized bed vessel by hot gases from a methane combustor. The sorbent (typically at 900 °F) enters a moving bed regenerator, countercurrent to methane introduced at the bottom of the reactor. An offgas containing sulfur dioxide (SO_2) is evolved. Copper oxide contained in the sorbent entering the regenerator may react rapidly with SO_2 in the exiting off-gas to form copper sulfite ($CuSO_3$) [15]:

$$CuO_{(s)} + SO_{2\,(g)} \rightarrow CuSO_{3\,(s)} \qquad (5)$$

Thus, just inside the regenerator, the sorbent may consist of copper oxide, copper sulfite and copper sulfate. Some tests have also indicated the presence of compounds such as Cu_2O and Cu_2SO_3 [15]. However, pending further studies to provide a design basis, these species are excluded from consideration in this analysis. It is assumed that copper sulfite, copper sulfate, and copper oxide are regenerated to copper with different regeneration efficiencies. The regeneration reactions are:

$$CuSO_{4\,(s)} + \frac{1}{2} CH_{4\,(g)} \rightarrow Cu_{(s)} + SO_{2\,(g)} + \frac{1}{2} CO_{2\,(g)} + H_2O_{(g)} \qquad (6)$$

$$CuSO_{3\,(s)} + \frac{1}{4} CH_{4\,(g)} \rightarrow Cu_{(s)} + SO_{2\,(g)} + \frac{1}{4} CO_{2\,(g)} + \frac{1}{2} H_2O_{(g)} \qquad (7)$$

$$CuO_{(s)} + \frac{1}{4} CH_{4\,(g)} \rightarrow Cu_{(s)} + \frac{1}{4} CO_{2\,(g)} + \frac{1}{2} H_2O_{(g)} \qquad (8)$$

Copper and copper sulfite leaving the regenerator are rapidly oxidized to copper oxide upon contact with oxygen in the transport air of the pneumatic transport system. These reactions are exothermic:

$$Cu_{(s)} + \frac{1}{2} O_{2\,(g)} \rightarrow CuO_{(s)} \qquad (9)$$

$$CuSO_{3\,(s)} + \frac{1}{2} O_{2\,(g)} \rightarrow CuSO_{4\,(s)} \qquad (10)$$

The regeneration offgas is sent to a Claus plant for elemental sulfur recovery. A portion of the SO_2 must be reduced with natural gas to produce the required quantity of hydrogen sulfide for the Claus reaction. The overall reaction is:

$$CH_{4\,(g)} + 2\ SO_{2\,(g)} \rightarrow 2\ S_{(l)} + 2\ H_2O_{(g)} + CO_{2\,(g)} \qquad (11)$$

The overall methane requirement is one-half the molar flow rate of sulfur dioxide in the offgas. A portion of this requirement is met by unreacted methane contained in the regenerator offgas.

ENGINEERING-ECONOMIC MODEL

The copper oxide process performance model developed by Frey [8,14] includes mass and energy balances for the fluidized bed absorber, sorbent heater, regenerator, sorbent transport system, and ammonia injection system. Models were also developed by Frey [8,17] to characterize the performance of an integrated sulfuric acid or elemental sulfur byproduct recovery plant, and the power plant air preheater. Over a dozen chemical species are traced throughout the system. These species include components of the flue gas, sorbent transport air, regenerator off-gas, and other process streams. The mass balances account for the stoichiometry and conversion rates of Equations (1) through (11). In some cases, such as for the sulfation and regeneration reactions, chemical kinetic models are employed. An energy balance for each process area is calculated based on the mass balance, heat of chemical reactions, and enthalpy data for each chemical species.

Direct capital costs, indirect capital costs, fixed operating costs, and variable operating costs have been modeled for each component of the copper oxide system [8]. The direct capital

Table 1. Selected Copper Oxide Process Design Assumptions and Model Results

PARAMETER	Values		
	Case 1	Case 2	Case 3
Absorber SO_2 Removal Efficiency, %	90.0	94.7	90.5
Sulfur Plant Recovery Efficiency, %	95.0	95.0	95.0
Claus Tailgas Recycle to Flue Gas	No	No	Yes
Overall SO_2 Removal Efficiency, %	85.5	90.0	90.0
NO_x Removal Efficiency, %	90.0	90.0	90.0
Regeneration Efficiency, %	80	80	80
Sorbent Copper Loading (wt-%)	7	7	7
Superficial Flue Gas Velocity (ft/s)	4.5	4.5	4.5
Expanded Bed Height (inches)	48	48	48
Available Cu/S Ratio	1.59	2.03	1.61
Total Cu/S Ratio	1.99	2.54	2.01
Relative Levelized Cost	0.97	1.11	1.00

costs include the absorber, solids heater, regenerator, solids transport, flue gas handling, incremental costs of air preheater modifications, and byproduct recovery plants. These costs are estimated using "capacity-exponent" scaling relationships based on key process parameters. Indirect costs, including engineering, design, supervision, contractor, construction expense, and contingencies, are estimated as percentages of total direct costs. Other items included in the total capital requirement are interest during construction, royalties, pre-production costs, inventory capital, initial chemicals, and land. Fixed operating costs include operating and maintenance labor, maintenance materials, and administrative labor. Variable operating costs include makeup sorbent, ammonia, methane, electricity, and credits for byproduct sales and recovered energy in the air preheater, which reduces coal consumption.

The copper oxide process, sulfuric acid plant, elemental sulfur recovery plant, and air preheater performance and cost models are implemented as part of the IECM. One of the features of the IECM is the capability to calculate the levelized costs of the total pollution control system for a coal-fired power plant. The levelized costs are estimated using methods described by the Electric Power Research Institute [11].

MODEL APPLICATIONS

The copper oxide process engineering-economic model is applied to four case studies. The first concerns alternative approaches to the integration of an elemental sulfur byproduct Claus plant with the copper oxide process. Selected design assumptions and model results are shown in Table 1. The sulfur recovery efficiency of the Claus plant is 95%, with unconverted sulfur emitted as SO_2 in the tailgas. Thus, the overall sulfur removal efficiency for 90% flue gas sulfur removal would be only 85.5%. Such a design, Case 1, is likely to be unacceptable compared to conventional FGD systems, which are capable of 90% or greater sulfur capture. Therefore, two options are considered which achieve 90% overall sulfur capture. In Case 2, the removal efficiency of the copper oxide process is increased to counter-balance the Claus plant tailgas emissions. In Case 3, the tailgas emissions are recycled to the flue gas just upstream of the absorber, and the absorber sulfur removal efficiency is increased slightly to achieve an overall 90% removal efficiency. A preliminary economic analysis indicates only a modest cost difference between Case 1 and Case 3, whereas Case 2 yields clearly the highest costs. The Case 3 design, which offers the benefit of five percent higher overall SO_2 removal with a modest three percent increase in levelized cost compared to Case 1, is adopted here as a reference case.

The second case study concerns the design assumptions about the sorbent bed height in the fluidized bed absorber. Figure 2 illustrates the decrease in sorbent circulation rate obtained from increases in bed height, due to sulfation kinetics. Costs, which are sensitive to sorbent circulation rate, also tend to decrease. However, the flue gas pressure drop and induced fan electricity requirements increase with bed height. The overall effect on levelized costs is a region of minimum cost from approximately 48 to 60 inches of bed height Above 60 inches,

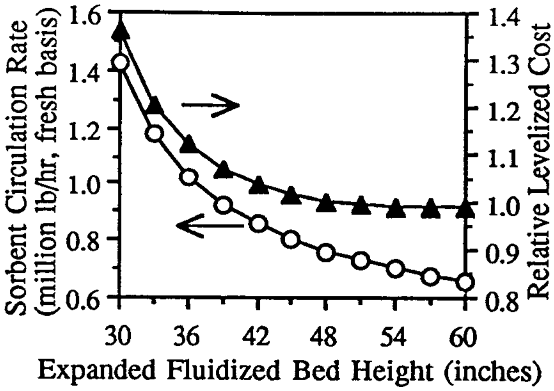

Figure 2. Sensitivity to Fluidized Bed Height.

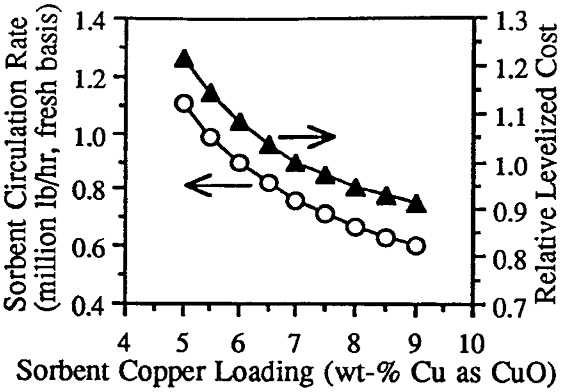

Figure 3. Sensitivity to Sorbent Copper Loading

levelized costs begin to increase. These results suggest that a four foot bed height may be optimal for a commercial-scale system, and would yield a 10 percent levelized cost savings compared to a 36 inch bed height.

The third case study illustrates the role of sorbent copper content as a design issue. The primary trade-off is between sorbent mass flow rate and sorbent attrition; however, the attrition characteristics of high copper sorbents are not well characterized. Data in Figure 3 point to the potential advantages of high copper loadings. Actual costs may tend to rise with high copper loadings due to the unaccounted for potential for high attrition.

A fourth area for process optimization is the sorbent regeneration efficiency. In Figure 4, all of the copper oxide entering the regenerator is assumed to be converted to copper sulfite, which is also assumed to have the same regeneration efficiency as copper sulfate. Modest cost savings may be obtained from higher regeneration efficiencies than the 80 percent reference case. However, substantial cost penalties could be incurred if regeneration efficiencies are lower. For example, if copper sulfite were formed in regeneration, it is quite likely that it would not be regenerated with as high an efficiency as copper sulfate. This, in turn, could lead to substantial penalties on the sorbent circulation rate and total process costs.

FUTURE WORK

The economic model of the copper oxide process developed previously will be updated based on new design and cost information. The new engineering-economic model will then be employed in a number of detailed case studies to evaluate alternative process designs and to characterize uncertainties in predicting performance and cost. A key aspect of the latter effort will be the explicit quantification of uncertainties using probability distributions and a variant of Monte Carlo simulation. The insights gained from the model will be used to identify promising design options and priorities for research and development efforts.

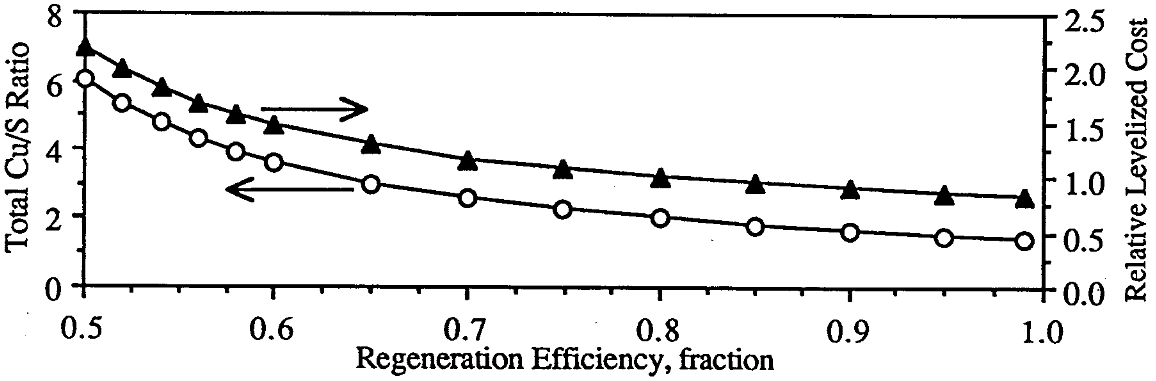

Figure 4. Sensitivity of the Total Cu/S Ratio and Levelized Cost to Regeneration Efficiency.

ACKNOWLEDGMENTS

The work described in this paper was sponsored by A.E. Roberts and Associates, Inc., under subcontract to UOP. UOP is the prime contractor for contract DE-AC22-85PC81004 of the U.S. Department of Energy's Pittsburgh Energy Technology Center. While the author is grateful to the sponsors and others that have provided information for this study, the author is solely responsible for the content and assumptions of this paper.

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