

Performance Model of the Fluidized Bed Copper Oxide Process for SO₂/NO_x Control

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INTRODUCTION

The fluidized bed copper oxide process is an advanced technology for controlling SO₂ 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 copper oxide 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 SO₂ and NO_x control: (1) it combines SO₂ 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

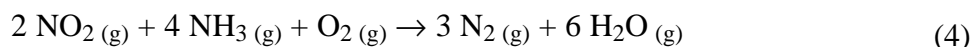
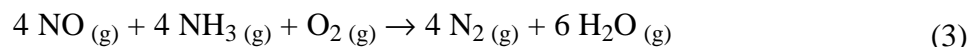
To evaluate the copper oxide process, a detailed performance and economic model was developed by Frey.⁸ This model was implemented as part of a broader modeling framework, the Integrated Environmental Control Model (IECM), developed by Rubin et al.^{9,10} The IECM includes performance, emissions, and 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 integrated environmental control strategies for coal-fired power plants. Details of the IECM's copper oxide process, power plant air preheater, sulfur recovery, and sulfuric acid recovery plant models are described elsewhere.^{8,10}

The models characterize mass and energy balances for key process equipment. Direct and indirect capital costs, variable and fixed operating costs, 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}

In this study, the performance model for the copper oxide process is updated to include new models for the kinetics of sulfation and regeneration, based on work by Harriott and Markussen¹⁴ and Harriott.¹⁵⁻¹⁸ The mass and energy balance for the sorbent are modified accordingly. The design basis for byproduct sulfur recovery and for calculating process energy requirements are also updated. The new performance model is applied to evaluate several design issues, including overall sulfur removal efficiency, fluidized bed absorber height, sorbent copper loading, and regeneration efficiency. Directions for future work are discussed.

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 from these exothermic reactions can be recovered via the power plant air preheater. The net chemical reactions occurring in the absorber are:



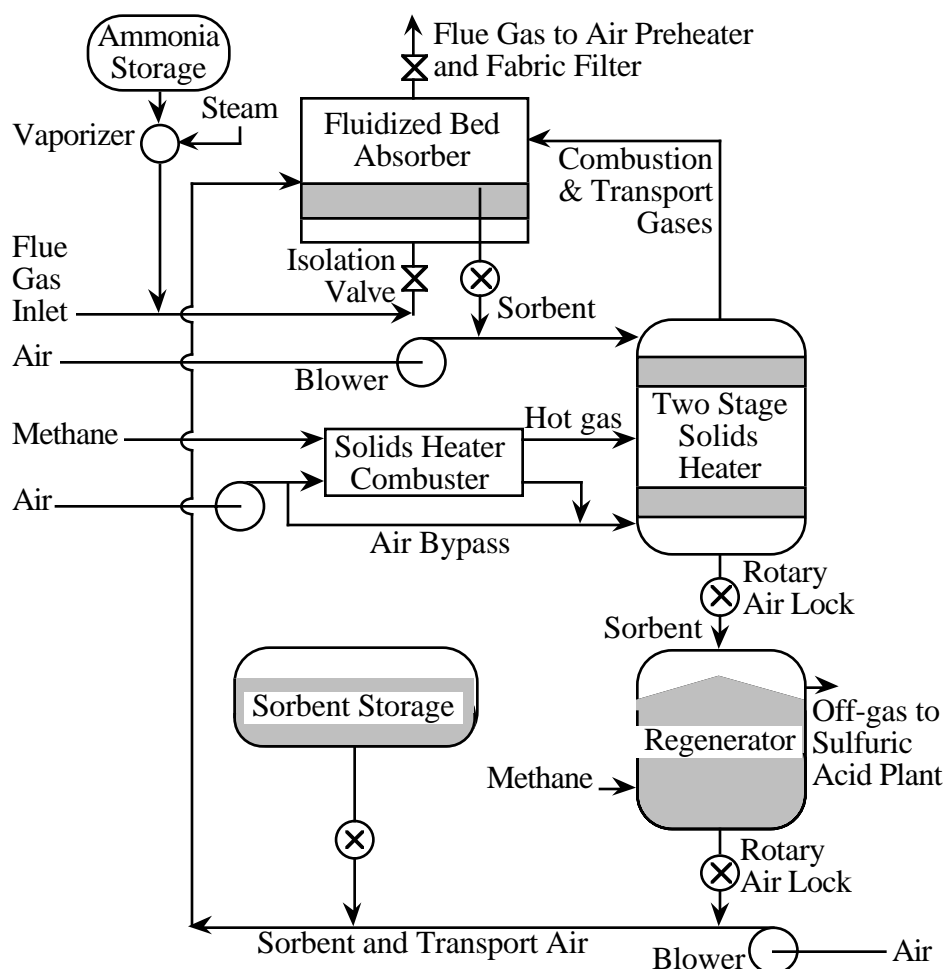


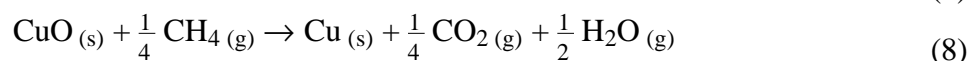
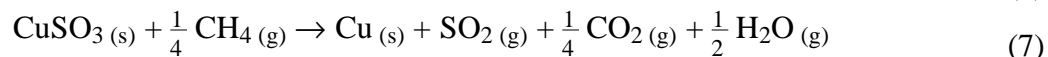
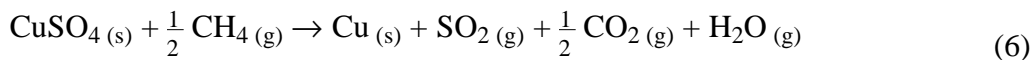
Figure 1. Schematic Diagram of the PETC Fluidized Bed Copper Oxide Process.

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 (SO₂) is evolved. Copper oxide contained in the sorbent entering the regenerator may react rapidly with SO₂ in the exiting off-gas to form copper sulfite (CuSO₃):¹⁴

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 Cu₂O and Cu₂SO₃.¹⁴ However, pending further studies to provide a design basis, these species are excluded from consideration in this model.

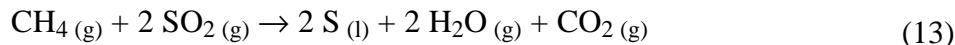
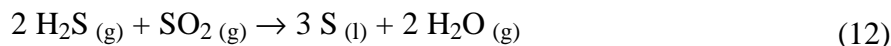
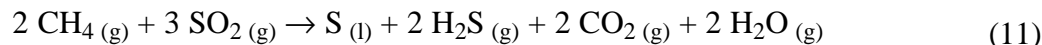
It is assumed that copper sulfite, copper sulfate, and copper oxide are regenerated to copper with efficiencies η_{r1} , η_{r2} , and η_{r3} , respectively. The regeneration reactions are:



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:



The regeneration offgas is sent to a Claus plant for elemental sulfur recovery. A portion of the SO₂ must be reduced with natural gas to produce the required quantity of hydrogen sulfide (Equation 11) for the Claus reaction (Equation 12). The overall reaction is given by Equation (13).



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.

NEW ANALYTICAL MODELS

New analytical models for the sorbent mass balance, the absorber sulfation reaction, regeneration, byproduct recovery, and energy penalties are derived.

Sorbent Mass Balance

To calculate the sorbent flow rate at the absorber inlet, a single equation that accounts for the key assumptions regarding process chemistry has been developed. The basis for the sorbent mass balance per mole of SO₂ in the flue gas is given in Table 1.

At the absorber inlet, the sorbent contains available copper (as copper oxide) and an unknown amount of copper sulfate, which is residual unregenerated copper from the previous absorption/regeneration cycle. A portion of the copper oxide reacts with SO₂ in the flue gas to form additional copper sulfate. The available copper-to-sulfur molar ratio, R, is estimated using a kinetics model described later. At the regenerator inlet, a fraction of the copper oxide may react with SO₂, evolved in the lower regions of the regenerator, to form copper sulfite. The copper oxide, copper sulfite, and copper sulfate are regenerated to copper. Harriott and Markussen¹⁴ suggest that the regeneration efficiency for copper sulfite may be substantially lower than for copper sulfate for a given residence time. Therefore, these efficiencies are parameterized for each species to permit sensitivity analysis. Upon contact with oxygen in the sorbent transport system, all of the copper and copper sulfite is assumed to be oxidized. The sorbent composition in the solids transport system is the same as that entering the absorber.

The mass balance is closed by solving for the unknown molar amount of copper sulfate entering the absorber per mole of SO₂:

$$R_{\text{CuSO}_4} = \frac{\eta_s (1-\eta_{r2}) + x_1 (1-\eta_{r1}) (R-\eta_s)}{\eta_{r2}} \quad (14)$$

The molar flow rate of any copper species at any point in the process can be calculated by multiplying the absorber inlet molar flow of SO₂ by the appropriate coefficient in Table 1. For example, the molar flow rate of copper oxide at the absorber inlet is given by:

$$M_{\text{CuO},A,i} = R \cdot M_{\text{SO}_x,A,i} \quad (15)$$

where: $M_{\text{SO}_x,A,i} = M_{\text{SO}_2,A,i} + M_{\text{SO}_3,A,i}$ (16)

The total amount of copper entering the absorber is greater than the available molar amount. The available copper to sulfur molar ratio is R, and the total copper to sulfur molar ratio is:

$$R_{\text{tot}} = R + R_{\text{CuSO}_4} \quad (17)$$

Table 1. Mass balance for sorbent in fluidized bed copper oxide process.

Location	Moles of Species per mole of SO ₂			
	Cu	CuO	CuSO ₃	CuSO ₄
Absorber Inlet	0	R	0	R _{CuSO₄}
Absorb. Outlet	0	(R-η _s)	0	(R _{CuSO₄} +η _s)
Just In Regen.	0	(1-x ₁) (R-η _s)	x ₁ (R-η _s)	(R _{CuSO₄} +η _s)
Regenerator Outlet	η _{r3} (1-x ₁) (R-η _s) + η _{r1} x ₁ (R-η _s) + η _{r2} (R _{CuSO₄} +η _s)	(1-η _{r3}) (1-x ₁) • (R-η _s)	(1-η _{r1}) x ₁ (R-η _s)	(1-η _{r2}) (R _{CuSO₄} +η _s)
Transport line and absorber inlet	0	R = (1-x ₁) (R-η _s) + η _{r1} x ₁ (R-η _s) + η _{r2} (R _{CuSO₄} +η _s)	0	R _{CuSO₄} = (1-η _{r1}) x ₁ (R-η _s) + (1-η _{r2}) • (R _{CuSO₄} +η _s)

A general formula is developed for calculating the sorbent mass flow as a function of the sorbent composition. The convention used in previous studies has been to define the sorbent composition based on the weight percent of copper, assuming that all of the copper is in the form of copper oxide. Therefore, the sorbent mass flow rate on an equivalent fresh sorbent basis is:

$$m_{s,\text{fresh}} = \left(\frac{MW_{Cu}}{W_{Cu}} \right) (M_{Cu} + M_{CuO} + M_{CuSO_3} + M_{CuSO_4}) \quad (18)$$

The actual sorbent mass flow is affected by the copper speciation. Factors must be included to account for the effect of different copper species on the sorbent mass flow rate. For example, for copper sulfate the mass flow rate is increased due to the mass differential between copper oxide and copper sulfate. The difference is calculated on a copper basis:

$$\Delta MW_{CuSO_4} = \frac{MW_{CuSO_4} - MW_{CuO}}{MW_{Cu}} = \frac{159.54 - 79.54}{63.54} = 1.26 \quad (19)$$

The effect of the weight difference is proportional to the weight fraction of copper (as equivalent copper oxide) in the sorbent. The general equation is therefore:

$$m_s = \left(\frac{MW_{Cu}}{W_{Cu}} \right) \{ (1-0.252W_{Cu})M_{Cu} + M_{CuO} + (1+1.007W_{Cu})M_{CuSO_3} + (1+1.26W_{Cu})M_{CuSO_4} \} \quad (20)$$

For example, the absorber inlet sorbent mass flow rate on a lb/hr basis can be calculated as:

$$m_{s,A,i} = \left(\frac{MW_{Cu}}{W_{Cu}} \right) \{ R + (1 + 1.260W_{Cu}) R_{CuSO_4} \} \cdot M_{SO_x,A,i} \quad (21)$$

While the sorbent mass flow at the absorber exit is given by:

$$m_{s,A,o} = \left(\frac{MW_{Cu}}{W_{Cu}} \right) \{ (R-\eta_s) + (1 + 1.260W_{Cu}) (R_{CuSO_4} + \eta_s) \} \cdot M_{SO_x,A,i} \quad (22)$$

The molar flow rate of the alumina oxide substrate is assumed to be the same at all points. This flow is calculated based on the absorber inlet sorbent mass flow:

$$M_{Al_2O_3} = \left(\frac{MW_{Cu}}{W_{Cu}} - MW_{CuO} \right) \left(\frac{1}{MW_{Al_2O_3}} \right) R_{\text{tot}} \cdot M_{SO_x,A,\text{in}} \quad (23)$$

Sulfation Reaction Model

Harriott^{15,16} has developed a kinetic model for the sulfation reaction assuming that the solids in the fluidized bed are perfectly mixed:

$$\ln\left(\frac{y_o}{y_i}\right) = -\alpha R y_i + \alpha (y_i - y_o) \quad (24)$$

where:

$$\alpha = \frac{k_s P \rho_s Z A}{F_s} \quad (25)$$

If we define SO₂ removal efficiency as:

$$\eta_s = \frac{y_i - y_o}{y_i} \quad (26)$$

then the sulfation model may be rewritten as:

$$R = \eta_s - \frac{\ln(1 - \eta_s)}{\alpha y_i} \quad (27)$$

The quantity ($\rho_s Z A$) in the kinetic parameter α is the sorbent bed inventory in the absorber. We note that the sorbent residence time is calculated based on the bed inventory and the feed rate:

$$t_{r,a} = \frac{\rho_s Z A}{F_s} \quad (28)$$

Thus, the term α is:

$$\alpha = k_s P t_{r,a} \quad (29)$$

The reaction rate constant, corrected for the sorbent copper loading, is given by Yeh:¹⁹

$$k_s = 1,573 \exp(-14.23 W_{Cu}) \exp\left(-\frac{2,417.6}{T}\right) \quad (30)$$

Test data reported by Yeh et al.²⁰ were used with Harriott's sulfation model to estimate the available Cu/S ratio. Figure 2 shows a comparison of the experimental and predicted Cu/S ratios. The comparison indicates that Harriott's model provides reasonable estimates of the Cu/S ratio. The model yields estimates typically within ± 10 percent of the experimentally measured values. The model appears to be somewhat conservative in predicting Cu/S ratios slightly higher than the experimentally measured results. The model results diverge most noticeable for the high Cu/S ratios, which represents testing with low (18 inch) fluidized bed heights. Such bed heights are unlikely for commercial scale designs.

As a prerequisite to estimating the sorbent bed inventory, the absorber bed area is calculated based on the flue gas volumetric flow rate and the reactor bed gas superficial velocity:

$$A = \left(\frac{G_{FG}}{60 V_s}\right) \quad (31)$$

The sorbent bed inventory ($\rho_s Z A$) and the sorbent feed rate should be calculated on a consistent basis to estimate the sorbent residence time. The simplest case is to base the calculations on equivalent fresh sorbent. Thus, the sorbent feed rate to be used in the sulfation model is:

$$F_s = \left(\frac{MW_{Cu}}{W_{Cu}}\right) \left\{ R + \left[\frac{\eta_s (1-\eta_{r2}) + x_1 (1-\eta_{r1}) (R-\eta_s)}{\eta_{r2}} \right] \right\} \cdot \left(\frac{M_{SO_x,A,i}}{60 \text{ min/hr}}\right) \quad (32)$$

The expanded sorbent density should be used to estimate the sorbent bed inventory. In order to develop an explicit sulfation equation for R, it is necessary to rewrite Equation (32) as:

$$F_s = a + b \cdot R \quad (33)$$

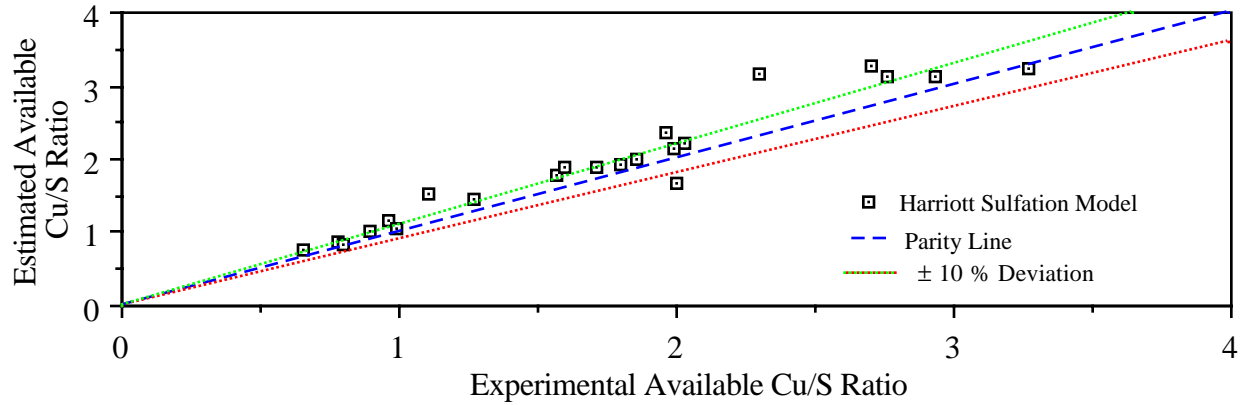


Figure 2. Comparison of Experimental and Model Results for Available Cu/S Ratio

where:

$$a = \left(\frac{MW_{Cu}}{W_{Cu}} \right) \left(\frac{M_{SO_x, A, i}}{60 \frac{\text{min}}{\text{hr}}} \right) \left[\frac{\eta_s (1 - \eta_{r2}) - x_1 \eta_s (1 - \eta_{r1})}{\eta_{r2}} \right] \quad (34)$$

$$b = \left(\frac{MW_{Cu}}{W_{Cu}} \right) \left(\frac{M_{SO_x, A, i}}{60 \frac{\text{min}}{\text{hr}}} \right) \left[\frac{\eta_{r2} + x_1 (1 - \eta_{r1})}{\eta_{r2}} \right] \quad (35)$$

We also define:

$$\hat{\alpha} = k_s P \rho_s Z A \quad (36)$$

$$\beta = \frac{\ln(1 - \eta_s)}{\hat{\alpha} y_i} \quad (37)$$

The sulfation model in Equation (27) is then rewritten in terms of the quantities in Equations (34), (35), (36), and (37):

$$R = \frac{\eta_s - a \beta}{1 + b \beta} \quad (38)$$

Regeneration Performance Model

The regenerator mass and energy balance model developed by Frey⁸ is revised to account for the potential formation of copper sulfite.^{14,17} A kinetic model developed by Harriott¹⁷ is used to estimate the residence time for regeneration of copper sulfate. A simplified response-surface model for residence time was developed based on statistical analysis of the model.

Regenerator Mass Balance. The mass balance for sorbent in the regenerator is given by Equation (14) and Table 1. At the regenerator inlet, the molar fraction of total copper in the sorbent which is in the form of copper sulfate is given by:

$$x_{CuSO_4} = \frac{(R_{CuSO_4} + \eta_s)}{R_{tot}} \quad (39)$$

The mass balance for gaseous species in the regenerator includes methane at the regenerator inlet, and regeneration off-gas containing methane, sulfur dioxide, carbon dioxide, and water vapor. The total amount of methane required for regeneration is estimated per Harriott¹⁷ based on the minimum requirement for 100 percent regeneration and a multiplier for excess methane. The minimum methane requirements are determined from the stoichiometry of Equations (6), (7) and (8). Thus, the total methane requirement is:

$$M_{CH_4, R, i} = R_{CH_4} [0.5x_{CuSO_4} + 0.25(1 - x_{CuSO_4})] R_{tot} M_{SO_x} \quad (40)$$

The amount of sulfur dioxide produced depends on the fraction of copper oxide converted to copper sulfite and the actual regeneration efficiencies for copper sulfite and copper sulfate. Water vapor is produced in all three of the assumed regeneration reactions. For each mole of water vapor produced, one-half mole of carbon dioxide is produced. The molar amount of methane consumed in the regenerator is the same as the molar amount of carbon dioxide produced. Thus, the composition of the offgas is:

$$M_{\text{SO}_2,\text{R},\text{o}} = [\eta_{\text{r}2} x_{\text{CuSO}_4} + (\eta_{\text{r}1} - 1) x_1 (1 - x_{\text{CuSO}_4})] R_{\text{tot}} M_{\text{SO}_x} \quad (41)$$

$$M_{\text{H}_2\text{O},\text{R},\text{o}} = \{ \eta_{\text{r}2} x_{\text{CuSO}_4} + 0.5 (1 - x_{\text{CuSO}_4}) [\eta_{\text{r}1} x_1 + \eta_{\text{r}3} (1 - x_1)] \} R_{\text{tot}} M_{\text{SO}_x} \quad (42)$$

$$M_{\text{CO}_2,\text{R},\text{o}} = 0.5 M_{\text{H}_2\text{O},\text{R},\text{o}} \quad (43)$$

$$M_{\text{CH}_4,\text{R},\text{o}} = M_{\text{CH}_4,\text{R},\text{i}} - M_{\text{CO}_2,\text{R},\text{o}} \quad (44)$$

Regenerator Energy Balance. Four chemical reactions (Equations 5-8) are assumed to occur. For the formation of copper sulfite (Equation 5), thermodynamic data are not available in the standard reference literature to calculate the heat of reaction. Harriott¹⁷ estimated the heat of reaction as $\Delta H_1 = -93,240$ Btu/lbmole CuO, based on data for SO₂ oxidation and CuSO₄ formation. Heats of reaction for the regeneration of copper sulfate and copper oxide (Equations (6) and (8), respectively) were estimated by Frey⁸ and are $\Delta H_2 = 30,700$ Btu/lbmole CuSO₄ and $\Delta H_3 = -19,380$ Btu/lbmole CuO, respectively. The heat of reaction for the regeneration of copper sulfite, ΔH_4 , was estimated, based on the heat of reactions for Equations 5 and 8, as $-73,860$ Btu/lbmole. The total heat of reaction for all chemical reactions in the regenerator is given by:

$$\begin{aligned} \Delta H_{\text{r,tot}} = & x_1 (1 - x_{\text{CuSO}_4}) \Delta H_1 + \eta_{\text{r}2} x_{\text{CuSO}_4} \Delta H_2 \\ & + \eta_{\text{r}3} (1 - x_1) (1 - x_{\text{CuSO}_4}) \Delta H_3 + \eta_{\text{r}1} x_1 (1 - x_{\text{CuSO}_4}) \Delta H_4 \end{aligned} \quad (45)$$

The total molar flow of solids entering the regenerator is:

$$M_{\text{s},\text{R},\text{i}} = M_{\text{Cu},\text{R},\text{i}} + M_{\text{CuO},\text{R},\text{i}} + M_{\text{CuSO}_3,\text{R},\text{i}} + M_{\text{CuSO}_4,\text{R},\text{i}} + M_{\text{Al}_2\text{O}_3,\text{R},\text{i}} \quad (46)$$

The solids enter at a specified temperature $T_{\text{R},\text{i}}$, which is the same as the solids heater outlet temperature. The average enthalpy of the solids entering the regenerator is given by:

$$\hat{h}_{\text{s}}(T_{\text{R},\text{i}}) = \frac{\sum M_{\text{j},\text{R},\text{i}} \hat{h}_{\text{j}}(T_{\text{R},\text{i}})}{\sum M_{\text{j},\text{R},\text{i}}} ; j = 1,5 \Rightarrow j = \text{Cu}, \text{CuO}, \text{CuSO}_3, \text{CuSO}_4, \text{Al}_2\text{O}_3 \quad (47)$$

The total molar flow and enthalpy of the solids at the regenerator outlet are similarly calculated.

Because thermodynamic data for copper sulfite are not available, the enthalpy of copper sulfite is estimated based on a multiplier and the enthalpy of copper sulfate:

$$\hat{h}_{\text{CuSO}_3}(\text{T}) = r_{\text{h}} \hat{h}_{\text{CuSO}_4}(\text{T}) \quad (48)$$

The value of the multiplier is estimated to be between 0.7 and 0.9, based on comparison of the specific heats of copper oxide, copper sulfate, sulfur dioxide, and oxygen at a temperature of 500 °C. A most likely value is assumed to be 0.8. This parameter can be treated as a probability distribution in the IECM pending development of thermodynamic data for copper sulfite.

The only inlet gas is methane, which enters at a temperature of $T_{\text{CH}_4,\text{R},\text{i}}$. The total molar flow of the off-gases is:

$$M_{\text{OG},\text{R},\text{o}} = M_{\text{SO}_2,\text{R},\text{o}} + M_{\text{H}_2\text{O},\text{R},\text{o}} + M_{\text{CO}_2,\text{R},\text{o}} + M_{\text{CH}_4,\text{R},\text{o}} \quad (49)$$

The off-gas is assumed to exit at the same temperature as the solids inlet. Therefore, the average enthalpy of the off-gas is given by:

$$\hat{h}_{OG}(T_{R,i}) = \frac{\sum M_{j,R,o} \hat{h}_j(T_{R,i})}{\sum M_{j,R,o}} ; j = 1,4 \Rightarrow j = SO_2, H_2O, CO_2, CH_4 \quad (50)$$

The only unknown to be calculated in the energy balance is the temperature of the sorbent leaving the regenerator. The energy balance is given by:

$$M_{s,R,o} \hat{h}_s(T_{s,R,o}) + M_{OG,R,o} \hat{h}_{OG}(T_{R,i}) + \Delta H_{r,tot} = M_{s,R,i} \hat{h}_s(T_{R,i}) + M_{CH_4,R,i} \hat{h}_{CH_4}(T_{CH_4,R,i}) \quad (51)$$

To facilitate an explicit equation for the sorbent outlet temperature, the term for the outlet sorbent molar flow and enthalpy can be rewritten as:

$$M_{s,R,o} \hat{h}_s(T_{s,R,o}) = M_{s,R,o} [\hat{h}_s(T_{R,i}) + c_{p,s} (T_{s,R,o} - T_{R,i})] \quad (52)$$

Thus, the temperature of the sorbent exiting the regenerator is given by:

$$T_{s,R,o} = T_{R,i} + \frac{M_{s,R,i} \hat{h}_s(T_{R,i}) + M_{CH_4,R,i} \hat{h}_{CH_4}(T_{CH_4,R,i}) - M_{s,R,o} \hat{h}_s(T_{R,i}) - M_{OG,R,o} \hat{h}_{OG}(T_{R,i}) - \Delta H_{r,tot}}{M_{s,R,o} c_{p,s}} \quad (53)$$

Regenerator Residence Time. A kinetic model developed by Harriott and Markussen¹⁴ and Harriott¹⁷ is used to estimate the residence time for the regeneration of copper sulfate. This model requires the development of a temperature profile within the regenerator. At a point "just inside" the regenerator, it is assumed that copper oxide has reacted to form copper sulfite. Thus, a mass and energy balance is developed for the uppermost portion of the regenerator in which this reaction occurs. The molar sorbent composition just inside the regenerator is calculated based on Table 1 and Equation 14. The gas composition just inside the regenerator is the same as at the regenerator outlet, with the exception of the SO₂ component due to the formation of copper sulfite:

$$M_{SO_2,R,JI} = [\eta_{r2} x_{CuSO_4} + \eta_{r1} x_1 (1 - x_{CuSO_4})] R_{tot} M_{SO_x,A,i} \quad (54)$$

The temperatures of the sorbent and the regeneration gases are assumed to be the same just inside the regenerator. Therefore, the temperature just inside the regenerator is:

$$T_{R,JI} = T_{R,i} + \frac{M_{OG,R,o} \hat{h}_{OG}(T_{R,i}) - M_{s,R,i} \hat{h}_s(T_{R,i}) + M_{s,R,JI} \hat{h}_s(T_{R,i}) - M_{OG,R,JI} \hat{h}_{OG}(T_{R,i}) + \Delta H_{r,JI}}{M_{OG,R,JI} c_{p,OG} - M_{s,R,JI} c_{p,s}}$$

where: $\Delta H_{r,JI} = x_1 (1 - x_{CuSO_4}) \Delta H_{r,1} R_{tot} M_{SO_x,A,i} \quad (55)$

An incremental mass and energy balance is calculated to estimate the temperature profile in the reactor. For each of n increments, the copper sulfate conversion is:

$$\Delta \eta_{r2} = \frac{\eta_{r2}}{n} \quad (56)$$

The conversion increments for regeneration of the other copper species are similarly defined. At the end of each regeneration increment, k (k=1,n), the sorbent composition is:

$$M_{Cu,R,k} = k \left\{ [\Delta \eta_{r3} (1 - x_1) + \Delta \eta_{r1} x_1] (R - \eta_s) + \Delta \eta_{r2} (R_{CuSO_4} + \eta_s) \right\} M_{SO_x,A,i} \quad (57)$$

$$M_{CuO,R,k} = [(1 - x_1) (1 - k \Delta \eta_{r3}) (R - \eta_s)] M_{SO_x,A,i} \quad (58)$$

$$M_{\text{CuSO}_3,\text{R},k} = [x_1 (1 - k \Delta\eta_{r1}) (R - \eta_s)] \cdot M_{\text{SO}_x,\text{A},i} \quad (59)$$

$$M_{\text{CuSO}_4,\text{R},k} = \left\{ (1 - k \Delta\eta_{r2}) (R_{\text{CuSO}_4} + \eta_s) \right\} \cdot M_{\text{SO}_x,\text{A},i} \quad (60)$$

The flow rates of the regeneration gases at the bottom (inlet) of each increment is given by:

$$M_{\text{SO}_2,\text{R},k} = \left\{ (1 - k) \Delta\eta_{r2} x_{\text{CuSO}_4} + [(1 - k) \Delta\eta_{r1} - 1] x_1 (1 - x_{\text{CuSO}_4}) \right\} R_{\text{tot}} M_{\text{SO}_x} \quad (61)$$

$$M_{\text{H}_2\text{O},\text{R},k} = (1 - k) \left\{ \Delta\eta_{r2} x_{\text{CuSO}_4} + 0.5 (1 - x_{\text{CuSO}_4}) [\Delta\eta_{r1} x_1 + \Delta\eta_{r3} (1 - x_1)] \right\} R_{\text{tot}} M_{\text{SO}_x} \quad (62)$$

$$M_{\text{CO}_2,\text{R},k} = 0.5 M_{\text{H}_2\text{O},\text{R},k} \quad (63)$$

$$M_{\text{CH}_4,\text{R},k} = M_{\text{CH}_4,\text{R},i} - M_{\text{CO}_2,\text{R},k} \quad (64)$$

The heat of reaction for each conversion step in the regenerator is:

$$\Delta H_{r,k} = \Delta\eta_{r2} x_{\text{CuSO}_4} \Delta H_2 + \Delta\eta_{r3} (1 - x_1) (1 - x_{\text{CuSO}_4}) \Delta H_3 + \Delta\eta_{r1} x_1 (1 - x_{\text{CuSO}_4}) \Delta H_4 \quad (65)$$

and the temperature is:

$$T_{\text{R},k} = T_{\text{R},k-1} + \left\{ \frac{M_{\text{OG},\text{R},k-1} \hat{h}_{\text{OG}}(T_{\text{R},k-1}) - M_{\text{s},\text{R},k-1} \hat{h}_{\text{s}}(T_{\text{R},k-1}) + M_{\text{s},\text{R},k} \hat{h}_{\text{s}}(T_{\text{R},k-1}) - M_{\text{OG},\text{R},k} \hat{h}_{\text{OG}}(T_{\text{R},k-1}) + \Delta H_{r,k}}{M_{\text{OG},\text{R},k} c_{\text{p,OG}} - M_{\text{s},\text{R},k} c_{\text{p,s}}} \right\} \quad (66)$$

The rate constant for the regeneration of copper sulfate is (Harriott, 1992c):

$$k_{\text{s},r} = \left\{ \begin{array}{l} 4.2 \times 10^7 \cdot F_w \cdot \exp\left(\frac{-21,700}{T}\right) \text{ if } T \leq 1,355 \text{ }^\circ\text{R} \\ 11.2 \times 10^5 \cdot F_w \cdot \exp\left(\frac{-16,800}{T}\right) \text{ if } T > 1,355 \text{ }^\circ\text{R} \end{array} \right\} \quad (67)$$

where the factor F_w is a correction based on the sorbent copper loading:¹⁸

$$F_w = 2.04 \exp(-14.23 W_{\text{Cu}}) \quad (68)$$

and the reaction rate is (Harriott, 1992c):

$$r_k = \frac{k_{\text{s},r,k} P_{\text{CH}_4,k} (\eta_{r2,\text{eq},k} - k \Delta\eta_{r2})}{1 + K_1 P_{\text{CH}_4,k} + K_2 P_{\text{SO}_2,k} + K_3 P_{\text{CO}_2,k}} \quad (69)$$

where: $\eta_{r2,\text{eq},k} = 1 - 0.9 P_{\text{CH}_4,k}$ (70)

The average reaction rate for each conversion interval is:

$$r_{k,\text{ave}} = \frac{r_{k-1} + r_k}{2} \quad (71)$$

and the total residence time required for regeneration of copper sulfate is:

$$t_{r,\text{CuSO}_4} = \sum_{k=1}^n \frac{\Delta\eta_{r2}}{r_{k,\text{ave}}} \quad (72)$$

Response Surface Model. A simplified response surface model for residence time was developed based on statistical analysis of the residence time model. Eight of the residence time model input parameters were assigned probability distributions representing possible ranges of values that might be expected in future model applications. These assumptions are given in Table 2. The distributions were sampled using Latin Hypercube sampling, a variant of Monte Carlo simulation, and the paired sets of sample values were used to calculate the corresponding residence

times. A total of 100 sets of calculations were made. Multivariate regression analysis was used to correlate the resulting distribution of residence time to each of the input distributions. Of the nine input parameters, seven were statistically significant. These key parameters exclude the regeneration efficiencies for copper oxide and copper sulfite. The simplified model for regenerator residence time is:

$$t_{r,CuSO_4} = 1.01 \cdot \exp\{8.31 + 0.10W_{Cu} - 0.009t_{s,R,i} + 0.90\eta_s + 3.76\eta_{r2} - 0.44x_1 - 0.39R - 1.03R_{CH_4}\} \quad (73)$$

This regression model has a coefficient of determination (R^2) of 0.95. The standard error of the estimate of residence time is 0.98 minutes. This model should not be extrapolated.

Table 2. Regenerator Residence Time Model Input Assumptions

Model Parameter	Deterministic (Nominal) Value	Probability Distribution	Values ^a
Methane Inlet Temperature	77 °F		
Sorbent Copper Loading	7 wt-%	Triangular	5,7,9 wt-%
Regenerator Inlet Temperature	900 °F	Triangular	850, 900, 910 °F
Absorber SO ₂ Removal Efficiency	90 %	Triangular	70, 90, 95 %
Copper Sulfate Regeneration Efficiency	80 %	Triangular	70, 80, 95 %
Copper Sulfite Regeneration Efficiency	40 %	Triangular	40, 40, 80 %
Copper Oxide Regeneration Efficiency	80 %	Triangular	70, 80, 95 %
Conversion of CuO to CuSO ₃	100 %	Uniform	0-100 %
Available Cu/S Ratio	1.3	Triangular	1.5, 2.0, 3.0
Excess Methane Ratio	$\eta_{r2} + .35$	Uniform	$\eta_{r2} + .10, \eta_{r2} + 1$

^a For uniform dist. actual ranges of values are shown. For triangular distrib., endpoints and mode are shown.

ByProduct Recovery

A two-stage Allied Chemical design is assumed for the Claus plant, based on previous studies.^{5,10} The sulfur recovery efficiency is 95 percent, with unconverted sulfur emitted as SO₂ in the Claus plant tailgas. Thus, the overall sulfur removal efficiency for 90 percent flue gas sulfur removal would be only 85.5 percent. Such a design is likely to be unacceptable compared to conventional FGD systems, which are capable of 90 percent or greater sulfur capture. Three approaches are possible to improve the overall system SO_x removal efficiency: (1) increase the copper oxide removal efficiency to compensate for the Claus plant tailgas emissions; (2) recycle the tailgas emissions to the flue gas upstream of the fluidized bed absorber, and adjust the copper oxide removal efficiency; or (3) increase the sulfur capture efficiency of the Claus plant. The third option is not considered here, due to the lack of readily available design information. However, the first two options are considered.

The first approach is easily modeled by adjusting the copper oxide sulfur oxides capture efficiency based on the sulfur plant recovery efficiency:

$$\eta_s = \frac{\eta_{s,overall}}{\eta_{Claus}} \quad (74)$$

The second approach is modeled by injecting an amount of SO₂, equivalent to the sulfur molar flow in the Claus plant tailgas, into the flue gas just upstream of the fluidized bed absorber:

$$M_{SO_2,recycle} = \left\{ \frac{(1 - \eta_{Claus}) \eta_s}{1 - (1 - \eta_{Claus}) \eta_s} \right\} M_{SO_2,FG} \quad (75)$$

$$\eta_s = \frac{\eta_{s,overall}}{\eta_{Claus} + (1 - \eta_{Claus}) \eta_{s,overall}} \quad (76)$$

As part of process integration, the regeneration offgas must be dried and cooled prior to entering the Claus plant.⁵ A typical offgas is at 875 to 910 °F, with 40 to 45 percent moisture. The design basis for gas inlet to the Claus plant calls for a temperature of 500 °F with six percent moisture. The net effect of the gas treatment is to generate superheated steam.

Energy Penalties and Credits

The copper oxide process consumes electricity to operate blowers associated with the pneumatic solids transport system and the sorbent heater combustor. Due to the flue gas pressure drop across the fluidized bed absorber, additional electrical energy is required to operate the power plant induced (ID) draft fan. The sulfur recovery system consumes a relatively small amount of power. The electrical requirements of the various fans are estimated using the "fan equation":²¹

$$EC_{\text{fan}} = \frac{\dot{Q} \Delta P}{8,512 \eta_{\text{fan}}} \quad (77)$$

An 85 percent fan efficiency is assumed. The ID fan incremental pressure drop is estimated based on the fluidized bed height.⁸ For the dense phase, regenerator to absorber solids transport system, the pressure drop is 22 psi.²² The sorbent transport pressure drop between the absorber and solids heater is 4.3 psi, and the combustor pressure drop is estimated at 90 inches of water.⁵⁻⁷

The copper oxide and sulfur recovery plants utilize methane (natural gas) for solids heating, sorbent regeneration, and regenerator offgas reduction, resulting in an energy penalty. Due primarily to the exothermic reactions occurring in the fluidized bed absorber, the flue gas temperature increase is typically on the order of 100 °F. This additional energy may be recovered via the power plant air preheater to increase the temperature of the combustion air entering the boiler. The calculation of this credit is described by Rubin et al.¹⁰ The copper oxide process uses steam for ammonia vaporization and injection. However, the offgas pretreatment section of the sulfur recovery plant produces steam, as previously described. Typically, the net effect is an energy credit. The thermal value of the steam is converted to an electricity equivalent basis using the power plant gross steam cycle heat rate (excluding the boiler).¹⁰

EXAMPLE APPLICATION

The copper oxide process performance model is applied to three case studies to compare alternative approaches for dealing with the Claus plant tailgas. The design basis is a 500 MW power plant. The coal composition and the calculated flow rate are given in Table 3, the calculated flue gas composition and flow upstream of the copper oxide process are given in Table 4, and the key design assumptions and modeling results for the three cases are given in Table 5. Case 1 represents a base case in which no measures are taken to correct for tailgas emissions. In Case 2, the SO₂ removal efficiency in the absorber is increased to compensate for the 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 percent removal efficiency. Cases 2 and 3 yield the same overall removal efficiency of 90 percent, while Case 1 achieves only 85.5 percent removal efficiency.

While the design basis for Case 1 is likely to result in inadequate overall sulfur emissions control, Case 2 is likely to result in prohibitive costs. The sorbent circulation is increased by 28 percent to achieve the 94.74 percent absorber sulfur removal efficiency needed to compensate for the Claus plant tailgas emissions. Due to the higher sorbent circulation rate, the methane requirement for solids heating and regeneration is increased, contributing to a larger net energy penalty on the power plant. In contrast, Case 3 achieves an overall sulfur removal efficiency of 90 percent with a modest increase in sorbent circulation rate of only six percent. Thus, Case 3 is clearly preferred over Case 2 for 90 percent overall sulfur control. The design basis for Case 3 is employed here for sensitivity analyses regarding absorber bed height, sorbent copper loading, and regeneration efficiency.

Table 3. Coal Composition and Model Results for Coal Input Flow Rate ^a

Component	Composition, (wt-% as fired)	Flow Rate (lb/hr)
Carbon	57.56	246,686
Hydrogen	4.14	17,743
Oxygen	7.00	30,000
Sulfur	3.12	13,371
Nitrogen	1.44	61,714
Ash	16.00	68,571
Moisture	10.74	46,029
TOTAL	100.00	428,571

^a Gross plant capacity is 500 MW with a gross cycle heat rate of 9,000 BTU/kWh.

Table 4. Model Results for Flue Gas Composition and Flow Rate ^a

Component	Composition (Volume %)	Flow Rate (lb/hr)	Flow Rate (lbmole/hr)
Nitrogen	73.229	3,091,870	110,371
Oxygen	3.217	155,175	4,849
Water Vapor	9.597	260,581	14,465
Carbon Dioxide	13.628	903,967	20,540
Sulfur Dioxide	0.260	25,129	393
Sulfur Trioxide	0.003	317	4
Nitrogen Oxide	0.062	2,810	10
Nitrogen Dioxide	0.003	227	5
TOTAL	100.000	4,440,070	150,720

^a 95% of the coal sulfur is emitted, with 99% as SO₂. Ambient air is at 80 °F and 65% relative humidity. Excess boiler air is 20%, and air preheater leakage is 19%.

The sorbent bed height has a direct effect on the fluidized bed sorbent inventory. The bed inventory is in turn a determinant of sorbent residence time in the regenerator, which affects the Cu/S molar ratio required to achieve a given removal efficiency. As the bed height increases, the sorbent circulation rate decreases, as shown in Figure 3. However, as the bed height increases, the flue gas pressure drop and the induced draft fan electricity requirements increase. Figure 3 indicates that a minimum net energy penalty is achieved at a fluidized bed height of approximately 40 inches. However, the energy penalty is not the sole determinant of cost. Much of the equipment in the copper oxide process, including the solids heater and regenerator, is sized based on the sorbent circulation rate. Therefore, a reduction in sorbent circulation rate can yield significant capital cost savings. Furthermore, operating costs are reduced due primarily to lower sorbent replacement costs and lower methane requirements to heat and regenerate the sorbent.

Optimization of the sorbent copper content is a key 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 4 point to the potential advantages of high copper loadings. Although the reaction rate constant (Equation 30) decreases with increased copper loading, the net effect is a substantial reduction in the sorbent circulation rate.

A third area for process optimization is the sorbent regeneration efficiency. Three case studies are considered in Figure 5. The first is a case in which none of the copper oxide entering the regenerator is converted to copper sulfite. Thus, the only reactions occurring are Equations (6) and (8). In the second case, all of the copper oxide entering the regenerator is assumed to be converted to copper sulfite. The regeneration efficiencies for copper sulfate and copper sulfite are assumed to be the same. This case yields results that approach those of the first case as the

Table 5. Copper Oxide Process Design Assumptions and Model Results

PARAMETER	Values		
	Case 1	Case 2	Case 3
Required SO ₂ Removal Efficiency, %	90.0	90.0	90.0
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
Net SO ₂ Captured, lbmole/hr	339	357	357
NO _x Removal Efficiency, %	90.0	90.0	90.0
NO _x Captured, lbmole/hr	88.7	88.7	88.7
Flue Gas Inlet Temp., °F	705	705	705
Flue Gas Outlet Temp., °F	797	812	801
Number of Absorbers	2	2	2
Area per Absorber, ft ²	3,898	3,898	3,898
CuO Regeneration Efficiency, %	80	80	80
CuSO ₄ Regeneration Efficiency, %	80	80	80
CuSO ₃ Regeneration Efficiency, %	80	80	80
Conversion of CuO to CuSO ₃ , frac.	1	1	1
Absorber Sorbent Inventory, lb	829,496	829,496	829,599
Sorbent Circulation Rate (lb/hr, fresh)	714,811	913,387	757,940
Absorber Inlet Sorbent Flow (lb/hr)	727,411	929,487	771,300
Sorbent Circ. Rate (lb fresh/1,000 scf)	12.5	16.0	13.2
Sorbent Absorber Residence Time (min)	70	54	66
Sorbent Copper Loading (wt-%)	7	7	7
Available Cu/S Ratio	1.59	2.03	1.61
Total Cu/S Ratio	1.99	2.54	2.01
Copper Utilization (S rem./avail Cu)	0.57	0.47	0.56
NH ₃ /NO _x Molar Ratio	1.00	1.00	1.00
Ammonia (lb/hr)	1,763	1,763	1,763
Ammonia Injection Steam (lb/hr)	1,129	1,129	1,129
Superficial Flue Gas Velocity (ft/s)	4.5	4.5	4.5
Expanded Bed Height (inches)	48	48	48
Fluidized Bed Pressure Drop (in. H ₂ O)	27.7	27.7	27.7
Bed Attrition (% of bed inventory)	0.020	0.020	0.020
Circ. Attrition (% of circulation)	0.047	0.047	0.047
Overall Attrition (% of circulation)	0.070	0.065	0.069
Makeup Sorbent (lb/hr)	508	603	528
Methane (lb/hr)	10,455	12,107	10,983
Net Energy Impact (kW)	17,108	18,308	17,640

regeneration efficiency approaches 100 percent. At 80 percent regeneration efficiency, the second case has a Cu/S ratio 15 percent greater than that of the first case. Finally, in the third case, the copper sulfite regeneration efficiency is assumed to be one-half that for copper sulfate. In this case, even at very high copper sulfate regeneration efficiencies, the unregenerated copper sulfite leads to a higher spent sorbent loading to the absorber and a correspondingly higher total Cu/S ratio than the other cases. These three cases illustrate that attention must be focused on understanding regeneration and its implications for process performance and economics.

FUTURE WORK

This paper has documented and illustrated new analytical performance models for the fluidized bed copper oxide process. This is a complex technology with many options for process optimization. In future work, the economic models developed previously will be updated based on

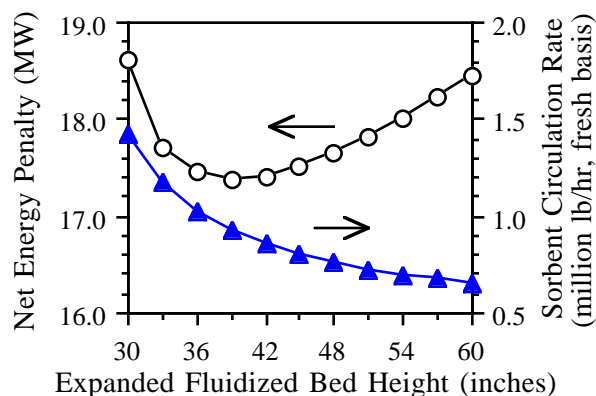


Figure 3. Sensitivity to Fluidized Bed Height.

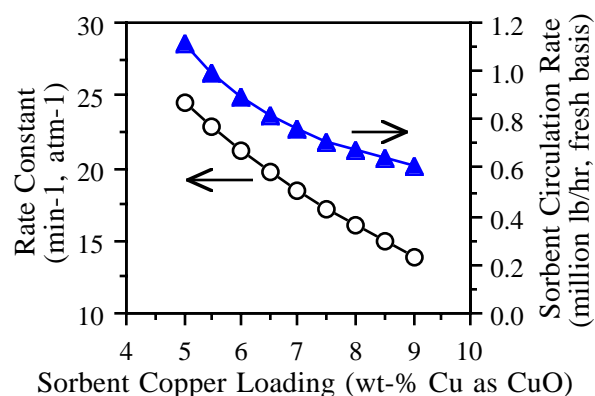


Figure 4. Sensitivity to Sorbent Copper Loading

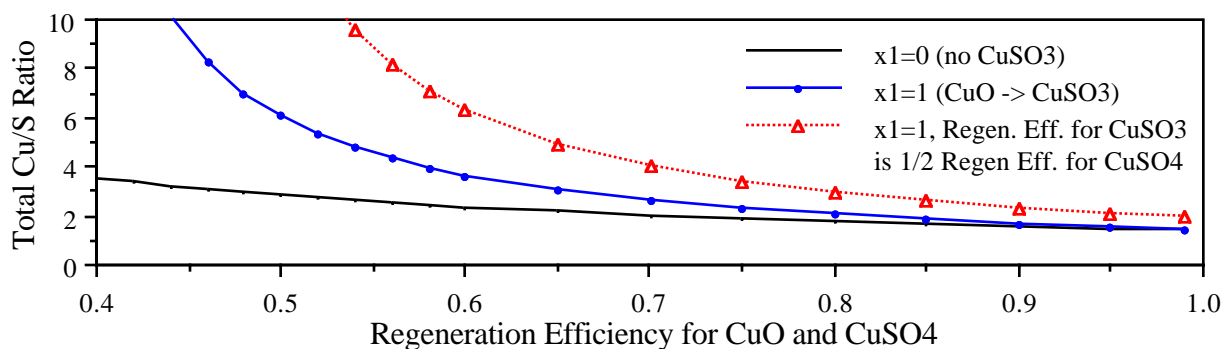


Figure 5. Sensitivity of the Total Cu/S Ratio to Regeneration Efficiency

new design and cost information. The new performance and economic models will then be employed in a number of case studies to evaluate alternative process designs and to characterize uncertainties in predicting performance and cost.

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NOMENCLATURE

A = Fluidized bed area, ft²
 EC_i = Energy consumption of device i, kW
 F_S = Fresh sorbent feed rate, lb/min
 G_{FG} = Flue gas flow rate, ft³/min
 h_i = Molar enthalpy of stream i, BTU/lbmole
 k_S = Reaction rate constant, 1/(min•atm)
 m_S = Sorbent mass flow rate, lb/hr
 M_i = Molar flow of species i, lbmole/hr
 M_{i,j,k} = Molar flow of species i at process area j's inlet or outlet k
 MW_i = Mole. wt. of species i, lb/lbmole
 P = Absorber inlet pressure, atm
 Q = Volumetric flow rate, ft³/min
 R = Available Cu to SO₂ molar ratio,

lbmole CuO/lbmole SO₂
 R_{CuSO₄} = CuSO₄ to SO₂ molar ratio, lbmole CuSO₄/lbmole SO₂
 t_{r,a} = Absorb. solids residence time, min
 T = Absorber bed temperature, K
 V_S = Superficial flue gas velocity, ft/sec
 W_{Cu} = Wt. frac. Cu as CuO in fresh sorbent, lb Cu/lb sorbent
 x = molar fraction of copper as copper sulfate at the regenerator inlet
 x₁ = molar fraction of copper oxide converted to copper sulfite.
 y_i = SO₂ inlet flue gas concentration, lbmoles SO₂/lbmole flue gas
 y_o = SO₂ outlet flue gas concentration, lbmoles SO₂/lbmole flue gas

Z = Fluidized bed height, ft

Greek Letter Symbols

ΔH = Heat of reaction, Btu/lbmole reactant

ΔP = Pressure drop (typically inches of H₂O)

α = Kinetic parameter (dimensionless)

η_{Claus} = Claus plant sulfur removal efficiency, fract.

η_{fan} = Fan efficiency, frac.

η_{r} = Overall sorbent regeneration efficiency, frac.

η_{r1} = Regen. efficiency for copper sulfite, frac.

η_{r2} = Regen. efficiency for copper sulfate, frac.

η_{r3} = Regen. efficiency for copper oxide, frac.

η_{s} = SO₂ removal efficiency, fraction

$\eta_{\text{s,o}}$ = Overall plant SO₂ removal efficiency, frac.

ρ_{s} = Sorbent density (expanded bed), lb/ft³

Subscripts

A = Absorber

FG = Flue gas

fresh = Sorbent on a fresh basis

i = Inlet

Jl = Just inside regenerator

o = Outlet

OG = Regenerator offgas

R = Regenerator

s = Sorbent

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