The Role of a Carbon Burnup Cell in Reducing SO_2 Emissions from Fluidized-Bed Coal Combustion Plants

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ABSTRACT

The role of a carbon burnup cell (CBC) in reducing limestone requirements to meet EPA SO_2 emission requirements for fluidized-bed coal combustor plants was investigated by evaluating laboratory scale experimental data. Four limestone feed options were analyzed: (1) fresh limestone fed only to a combustor, (2) fresh limestone fed to both a combustor and a CBC, (3) fresh limestone fed to a CBC, after which the partially sulfated limestone from the CBC is fed to a combustor, and (4) fresh limestone fed to a combustor and a portion of the partially sulfated (in the combustor) limestone injected into the CBC. For Greer limestone the calculations predict that options 2 and 4 would require approximately one-half as much limestone as do options 1 and 3.

The reactivities of Tymochtee dolomite and Germany Valley limestone with SO_2 were compared with that of Greer at identical conditions. Tymochtee dolomite is more reactive than Greer. Germany Valley, being a high-calcium limestone, has poor reactivity and with any of the limestone feed options would require high Ca/S ratios to meet the EPA SO_2 standard. Again, options 2 and 4 were more favorable for Tymochtee and Germany Valley stones.

INTRODUCTION

Atmospheric-pressure fluidized-bed combustion (AFBC) is one of the new methods being considered for producing power while meeting EPA SO_2 emission standards with high-sulfur coal. In this process, coal is burned at 850-950°C in a fluidized bed consisting of partially sulfated solid SO_2-sorbent particles. Limestones (or dolomites) are usually the bed material of choice due to their high calcium content, (which is highly reactive with SO_2 at these temperatures), low cost, and good availability.

To reduce the size and cost of an AFBC, a high superficial gas velocity (3-4.6 m/s) is required. However, high gas velocities cause high dust loadings (limestone and unburned coal) in the effluent gas stream. High gas velocities, therefore, produce low combustion efficiencies. Pope, Evans and Robbins (PER)[1] have reported combustion efficiencies of ∿85% at a fluidizing gas velocity of 3.8 m/s. To increase the overall combustion efficiency PER has incorporated into their process a carbon burnup cell (CBC) which operates at a higher temperature than the combustor and a lower fluidizing gas velocity (∿1100°C, 1.8 m/s). Unburned coal dust removed from the combustor effluent stream by cyclones is injected into the CBC. Pope, Evans and Robbins estimates that the overall combustion efficiency can be increased to approximately 99%.[1]

It has been estimated by Babcock and Wilcox[2] that the percentage of unburned sulfur in the elutriated coal dust from the combustor is ∿50% of the percentage of unburned coal. Thus, at a combustion efficiency of 85% in the combustor, approximately 93% of the sulfur in the coal is oxidized to SO_2 in the combustor; the other 7% is unburned and leaves the combustor in the coal dust with the effluent gas stream. Conflicting results[3,4] have been found by investigators as to the fate of this sulfur which will be released as SO_2 in the CBC. The National Coal Board[4] has found that the SO_2 reactivity of several limestones dramatically decreased above 1870°C. However, PER[3] found that the addition of limestone 1359 to their CBC caused a 2/3 reduction in SO_2 emissions. Due to the high operating temperature (1100°C) in the CBC, this SO_2 may not be captured by either partially sulfated limestone or fresh limestone injected into the CBC. This would cause 7% of the sulfur to bypass the sulfur-removal system of the combustor and be released as SO_2 in the CBC. Consequently, a greater percentage of the sulfur (which is released as SO_2) in the combustor must be captured to meet the EPA SO_2 standard (1.2 lb SO_2/million BTU produced by the entire system). Because of the increased required sulfur retention in the boiler, a greater overall Ca/S feed ratio would be required (as sulfur retention increases, calcium utilization decreases). Thus, if it is assumed that no sulfur is retained in the CBC, much greater amounts of limestone would be required to meet the EPA SO_2-emission standards.

The presently available experimental results[3,4] and analyses[5] of sulfur captive in the CBC are ambiguous. It is the purpose of this paper to clarify the role of the CBC in reducing SO_2 emissions from fluidized-bed coal combustor plants. The reactivities of fresh and partially sulfated limestones with SO_2 were determined on a TGA at the operating conditions of a combustor and a CBC. This information was used to predict limestone requirements to meet EPA standards with FBC systems for four limestone feed options.

EXPERIMENTAL

A thermogravimetric analyzer (TGA) was used to study the reaction of various limestones with SO_2 and O_2. A 0.3% SO_2 - 5% O_2 in N_2 synthetic combustion gas was used for all reactions. The limestone-SO_2 reactions were performed at either 900 or 1100°C to represent the operating temperatures for the combustor and CBC respectively. Fresh limestones before being sulfated at 900°C were precalcined in 20% CO_2 (balance N_2). The TGA system has been described in detail elsewhere.[6]

Three limestones were studied: (1) Tymochtee dolomite, a highly reactive stone, which contains 52% $CaCO_3$ and 43% $MgCO_3$, (2) Greer limestone, which contains 80% $CaCO_3$, 3.5% $MgCO_3$, 10% SiO_2, and a high sodium content (Na_2O, ∿0.23%), and is highly reactive compared with high-calcium limestones, and (3) Germany Valley limestone containing 98% $CaCO_3$ 0.6% $MgCO_3$, which is a high-calcium limestone with low reactivity. Data obtained with Greer limestone, which is being used in the 30-MWe AFBC pilot plant by PER, was used in the comparison of the various process options. The SO_2 reactivities of Tymochtee dolomite and Germany Valley limestone were compared with the reactivity of Greer.

RESULTS AND DISCUSSION

Four design options for feeding limestone into an AFBC power plant are considered (Fig. 3). In option 1, limestone is fed only to the combustor. In option 2, virgin limestone, is fed to both the combustor and the CBC. Virgin limestone is fed only to the CBC in option 3; the partially sulfated bed material from the CBC is then fed to the combustor. In the fourth option, fresh limestone is fed to the combustor and a portion of the partially sulfated limestone from the combustor is fed to the CBC.

In order to determine the limestone requirements for these four options, the reactivities of fresh and partially sulfated limestones with SO_2 were determined using a TGA (as described in the previous section). These results are shown in Fig. 1 for Greer limestone. Virgin limestones were reacted with SO_2 and O_2 at both 900 and 1100°C to determine the reactivity of fresh limestone at the conditions prevailing in a combustor and CBC (curves 2 and 3 respectively). These experiments provided the information necessary to determine limestone requirements for options 1 and 2 and parts of options 3 and 4. Limestones which had been partially sulfated (5% conversion of CaO to $CaSO_4$ and heat treated for 30 min at 1100°C) were reacted with SO_2 at 900°C to determine the combustor limestone requirements for option 3 (curve 4). A total heat-treating time of 30 min was chosen to simulate the estimated limestone CBC residence time. For option 4 consideration, fresh limestones were partially sulfated (reacted for 30 min with SO_2) at 900°C. This material was then tested for SO_2 reactivity at 1100°C (curve 5).

The initial reactivity of Greer Limestone at 900°C is higher than at 1100°C as expected, however, the extent of conversion of CaO to $CaSO_4$ after three hours is the same. Partially sulfating (5% conversion) of Greer limestone at 1100°C had a deterimental effect on its reactivity at 900°C (discussed later). Partially sulfated (at 900°C) Greer limestone at 1100°C had the highest reactivity. Total conversion of Ca to $CaSO_4$ (900 and 1100°C) was 58%. These results show that Greer limestone does react with SO_2 at 900 or 1100°C. However, this information is not in a useful form to predict limestone requirements for FBC plants. This information can be converted to the proper form which is a plot of internal SO_2 reduction (ratio of absorbed SO_2 to that released in the reactor) *vs* internal Ca/S ratio

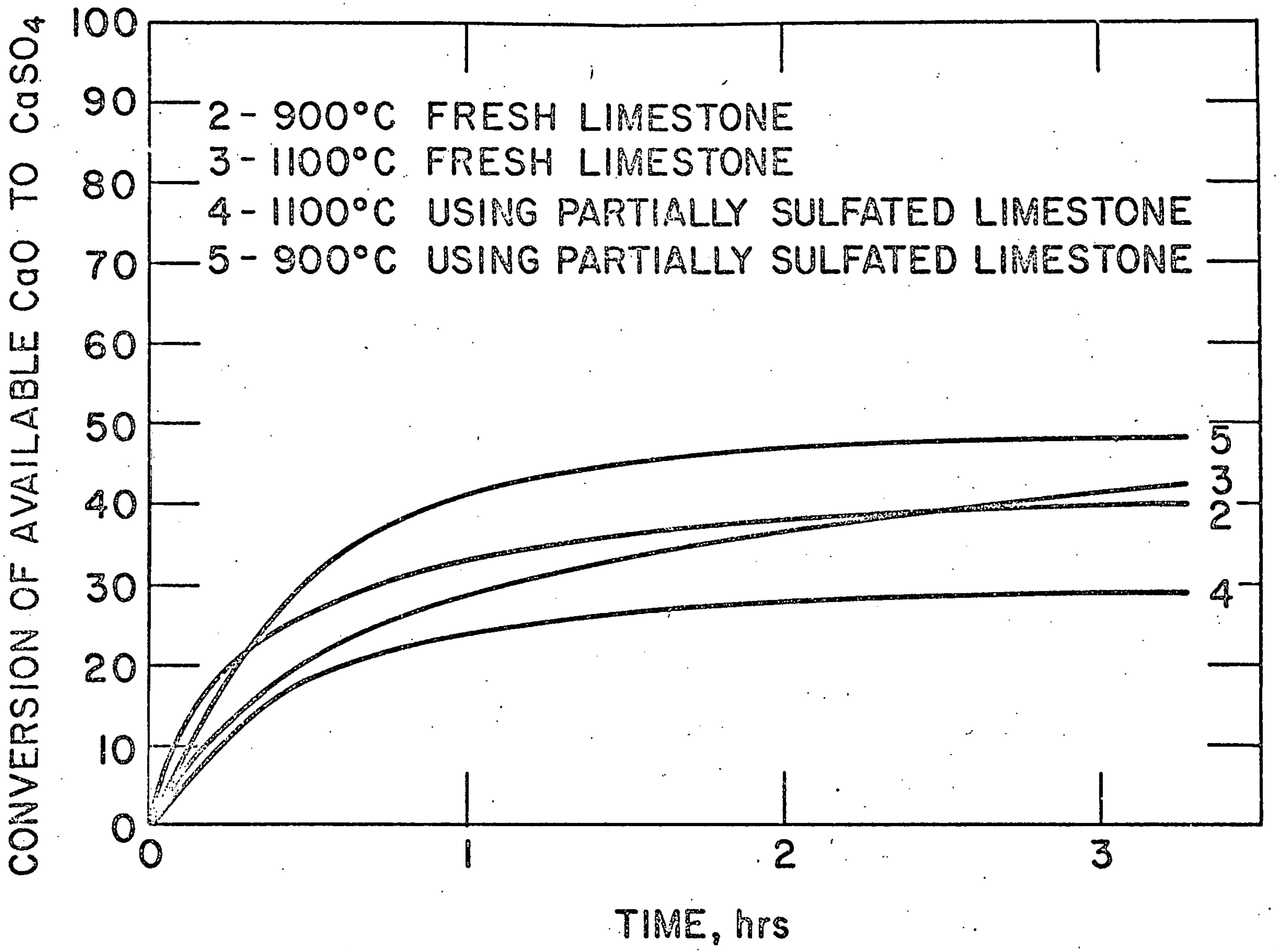

Fig. 1. Conversion of CaO to $CaSO_4$ in fresh or partially sulfated Greer limestone at 900° and 1100°C.

(S is the number of moles of sulfur released in the reactor), by using a fluid-bed desulfurization equation developed by Westinghouse.[7]

$$U = \frac{1}{Ca/S} \left[1 - \frac{V}{kH\varepsilon} \left(1 - e^{\frac{-kH\varepsilon}{V}} \right) \right] \qquad (2)$$

where U = calcium utilization, fraction

Ca/S = calcium to sulfur mole ratio

V = superficial gas velocity, m/sec

H = fluidized-bed height, m

ε = bed voidage, assumed to be 0.5

k = average particle reaction rate constant, Sec^{-1}.

This fluid-bed desulfurization equation gives the calcium utilization as a function of the "average" reaction rate constant of the particles in the bed (provided the superficial gas velocity and bed height are known). Thus, in order to determine U, the "average" rate constant, k must be known (which is obtained using the kinetic information shown in Fig. 1. See references 6 and 7 for calculation details.)

The results of the conversion of the kinetic data to SO_2 reduction *vs* Ca/S ratio for Greer limestone are shown in Fig. 2. (PER experimental results are also included.) The internal SO_2 reduction should be distinguished from SO_2 reduction, as is normally reported by FBC workers. This SO_2 reduction, as is conventionally reported, is the percentage of the total sulfur that does not leave the combustor as SO_2. That is, it includes both sulfur captured by the limestone and unburned sulfur and is not useful for the process analysis presented below. Curve 1 in Fig. 2 represents the corrected (internal) experimental results obtained by PER[8] using Greer

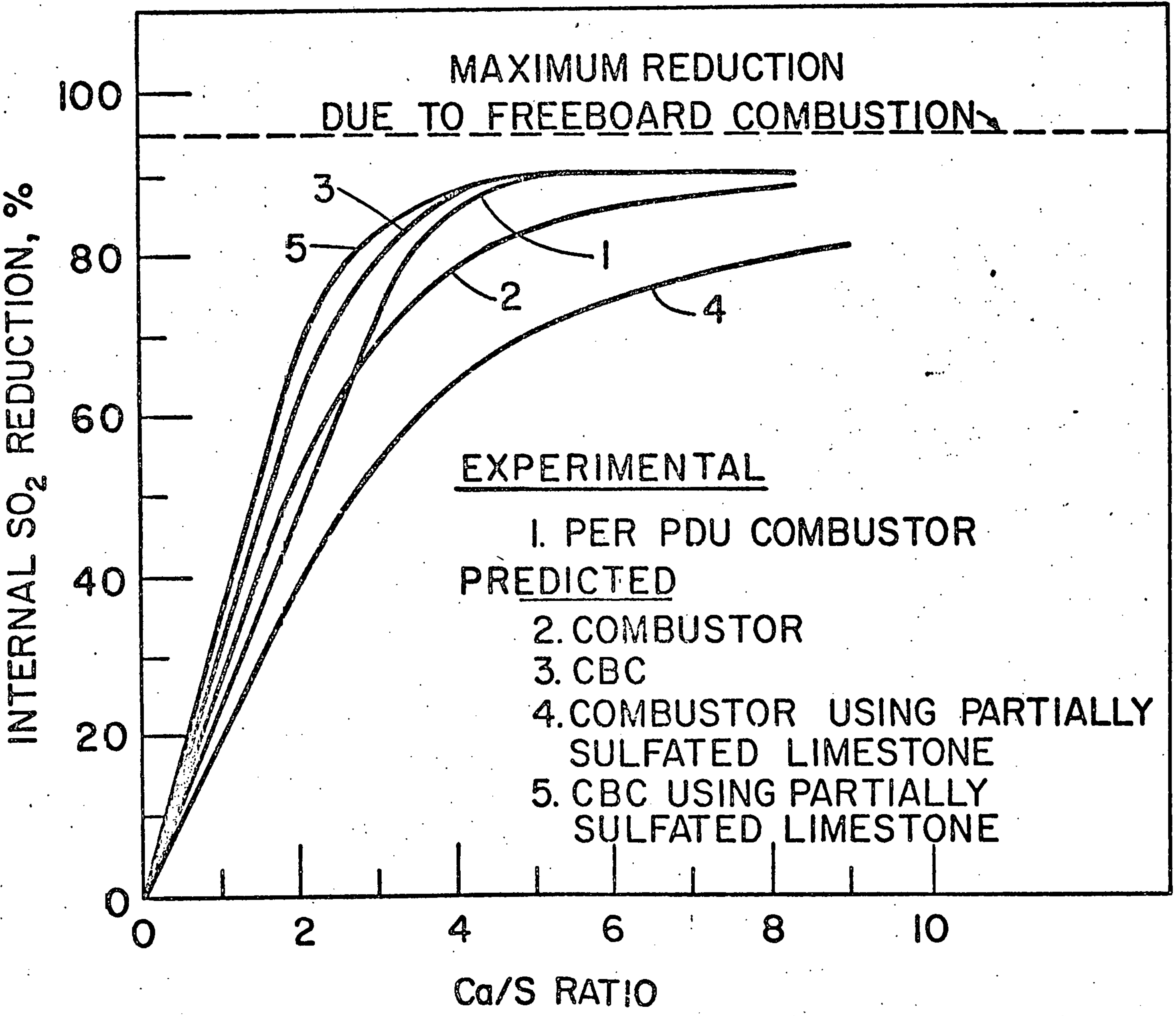

Fig. 2. Sulfur Reduction *vs* Ca/S Ratio.

limestone in the combustor assuming that 7% of the total sulfur remains in the unburned coal dust.

Curve 2 is the predicted results for Greer, based on the laboratory (TGA) experimental data. The laboratory experimental results predict a somewhat higher Ca/S requirement (Curve 2) for a given SO_2 reduction than has been found in PER's pilot plant (Curve 1). The laboratory results (Curve 2) were, nevertheless, used as a basis for comparing the four plant limestone feed options. The resulting comparisons are qualitatively correct; quantitative comparison can be made as sufficient FBC data becomes available. Curve 3 shows a higher SO_2 reduction for a given Ca/S ratio for fresh limestone in the CBC than in the combustor even though the SO_2 reactivity is lower in the CBC (Fig. 1). This is because the fluidizing velocity is lower in the CBC producing a longer SO_2 residence time in the fluid bed, thus allowing more SO_2 to be captured by the limestone.

Curve 4 projects a lower SO_2 retention in the combustor when Greer limestone is used that has been partially sulfated in the CBC. This is due to its low SO_2 reactivity (Fig. 1, Curve 4). It has been shown[9] that limestones which contain small quantities of $CaSO_4$ sinter rapidly at high temperatures (1100°C). Sintering causes small pores to coalesce into large pores, and a loss in total porosity results.[9] This sintered limestone now has a low SO_2 reactivity compared to fresh limestone at combustor conditions (900°C). This reactivity loss by the sintered limestone is however only experienced at the lower temperature (900°C). Although sintering does occur at the higher temperature, it is speculated that mobility of $CaSO_4$ within the limestone particle at the high temperature allows continued reaction of fresh calcium with SO_2, and thus the limestone retains its reactivity at the higher temperature (see Curve 3, Fig. 1 and 2). However, removing the limestone from the CBC (∿1100°C) and injecting it into the combustor at the lower temperature (∿900°C) causes a loss of $CaSO_4$ mobility in the partially sulfated and sintered limestone. With lower availability of CaO (reduced porosity and $CaSO_4$ mobility), the limestone is less reactive.

Curve 5 (Fig. 1 and 2) shows the highest limestone-SO_2 retention for given CaO/S ratio. Curve 5 represents the reactivity of partially sulfated (900°C) Greer in the CBC for option 4. Calcination at the lower temperature (900°C) produces a pore structure which is somewhat more favorable to the SO_2 diffusion-reaction process. It is expected that removing the partially sulfated limestone from the combustor and injecting it into the CBC causes the $CaSO_4$ to become more mobile. This exposes fresh calcium for reaction with SO_2.

EVALUATION OF AFBC SULFUR REMOVAL SYSTEM OPTIONS

The SO_2 reduction results in Fig. 2 were used to determine the overall limestone requirements for the four process options. The requirements for Greer limestone are given in Fig. 3. The required SO_2 removal in these calculations was based on using Sewickley Coal, a Pittsburg seam coal (4.3% S) which has a heating value of 12,200 Btu/lb. This coal requires an overall SO_2 retention of 83% to meet EPA SO_2 emission standards.

It was assumed in option 1 that there is no SO_2 retention by limestone (fresh, elutriated, or otherwise) in the CBC. This assumption, which is now known to be invalid, was used as a base case since as discussed in the introduction it has been a prevailing assumption in FBC research which would require high (but unknown) limestone requirements. Since 7% of the

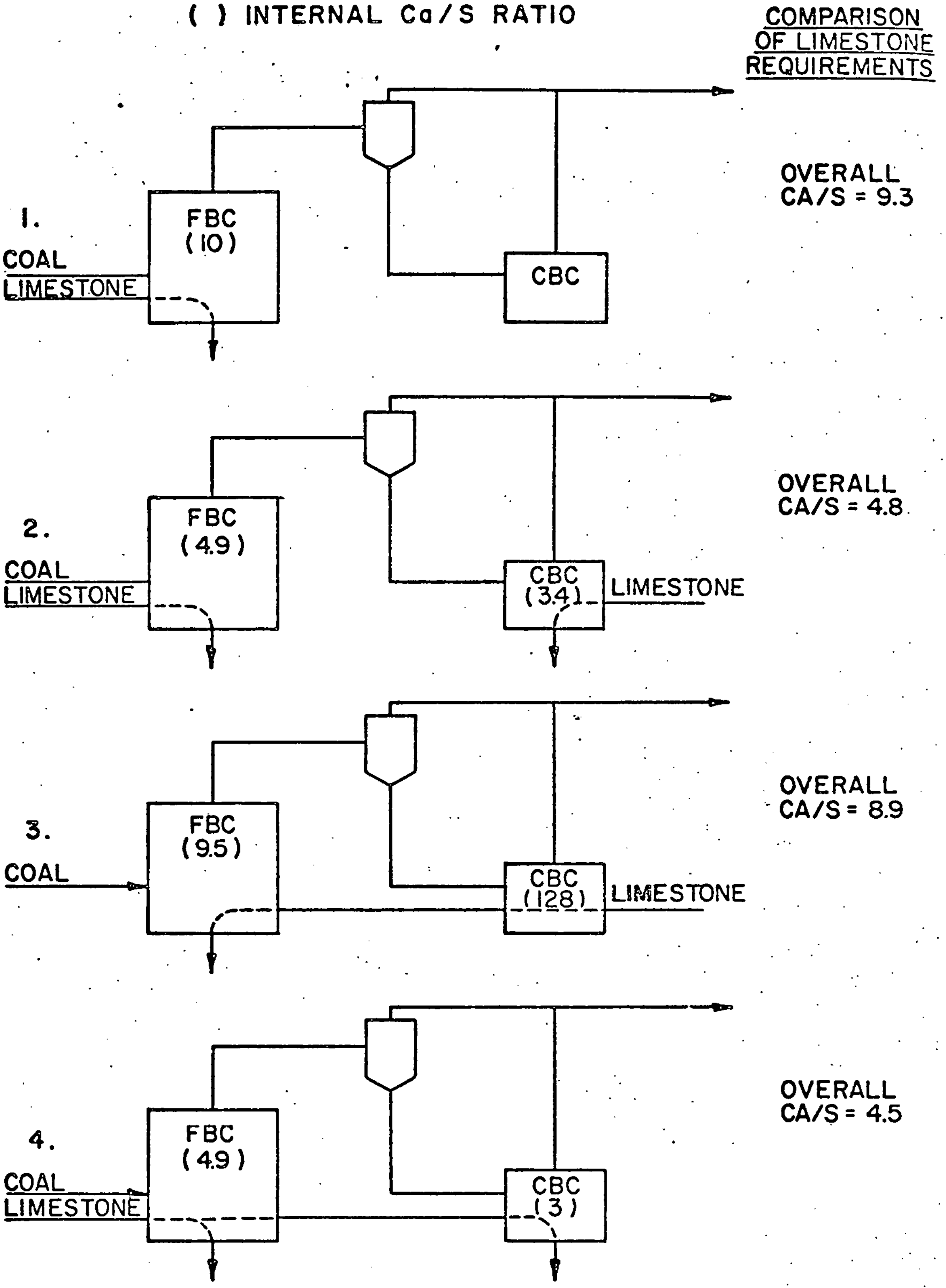

Fig. 3. Greer Limestone Requirements for Various Limestone Feed Schemes.

total sulfur is assumed to be released from the CBC as SO_2,[2,3] 89.3% SO_2 retention would be required in the combustor to give an overall SO_2 retention of 83%. This would require a Ca/S ratio in the combustor of 10 (curve 2, Fig. 2) and an overall Ca/S ratio of 9.3 (Fig. 3).

The limestone requirements can be decreased by feeding fresh limestone to the CBC to remove the SO_2 released in the CBC (option 2). A Ca/S ratio of 3.4 is required to achieve 83% SO_2 retention in the CBC (Fig. 2, curve 3). A Ca/S ratio of 4.9 (83% SO_2 retention) is required in the combustor (Fig. 2, curve 2). The overall Ca/S ratio is then 4.8, approximately one-half that for option 1.

The third option was considered in the hope that the high temperature in the CBC would have a beneficial heat treatment effect and that the CBC would have two roles, capture of SO_2 released in the CBC and pretreatment of limestone for limestone-SO_2 reactivity enhancement. As shown in Fig. 1 and 2, reactivity enhancement was not realized due to the detrimental effect of the $CaSO_4$ and high temperature (discussed above). Since in option 3 all virgin limestone is fed to the CBC, the Ca/S ratio is 128 and a 95% SO_2 retention would be obtained in the CBC. This would require an internal SO_2 retention of 82% in the combustor. Since stones that have been partially sulfated at high temperature (∿1100°C in the CBC) are less reactive at the lower temperature (Fig. 2, curve 4), a high internal CaO/S ratio (9.5) would be required in the combustor. The overall Ca/S feed ratio for option 3 is 8.9.

The fourth option provides a partially sulfated limestone feed stream from the combustor to the CBC. A CaO/S ratio of only 3 is required to obtain 83% SO_2 retention in the CBC, necessitating a Ca/S of 4.9 in the combustor. This option gives the lowest overall Ca/S feed ratio--4.5.

A detailed mass balance for option 4 is given in Fig. 4 for Ca and S through the system, since this feed option had the lowest limestone requirements. This mass balance was based on Greer limestone and 100 Kg of coal. Four kilograms of the sulfur converts to SO_2 in the combustor; the other 0.3 kilograms remains in the unburned coal and is injected into the CBC, where 83% or 0.28 Kg of the sulfur is captured by limestone that has been partially sulfated in the combustor. In the combustor, 3.3 Kg of the sulfur is captured by the limestone.

The limestone requirements presented above are based on Fig. 2. The projected limestone requirements are fairly insensitive to the SO_2-limestone reactivity in the CBC (Curves 3 and 5) since only 7% of the total sulfur is released as SO_2 in the CBC. Thus, if these SO_2 retention curves are over optimistic by a factor of 2, the error in the overall estimated Ca/S ratio would be low by only 4%. The overall Ca/S ratio is sensitive to the limestone-SO_2 reactivity in the combustor (curve 2) which is why fresh limestone-SO_2 reactivity at 900°C is used as a base case for comparing the various process options.

The results in Fig. 3 are for idealized limestone feed options which were chosen to elucidate the role of the CBC in minimizing limestone requirements. In actuality, unreacted and partially sulfated limestone will be elutriated with the unburned coal, removed from the gas by the

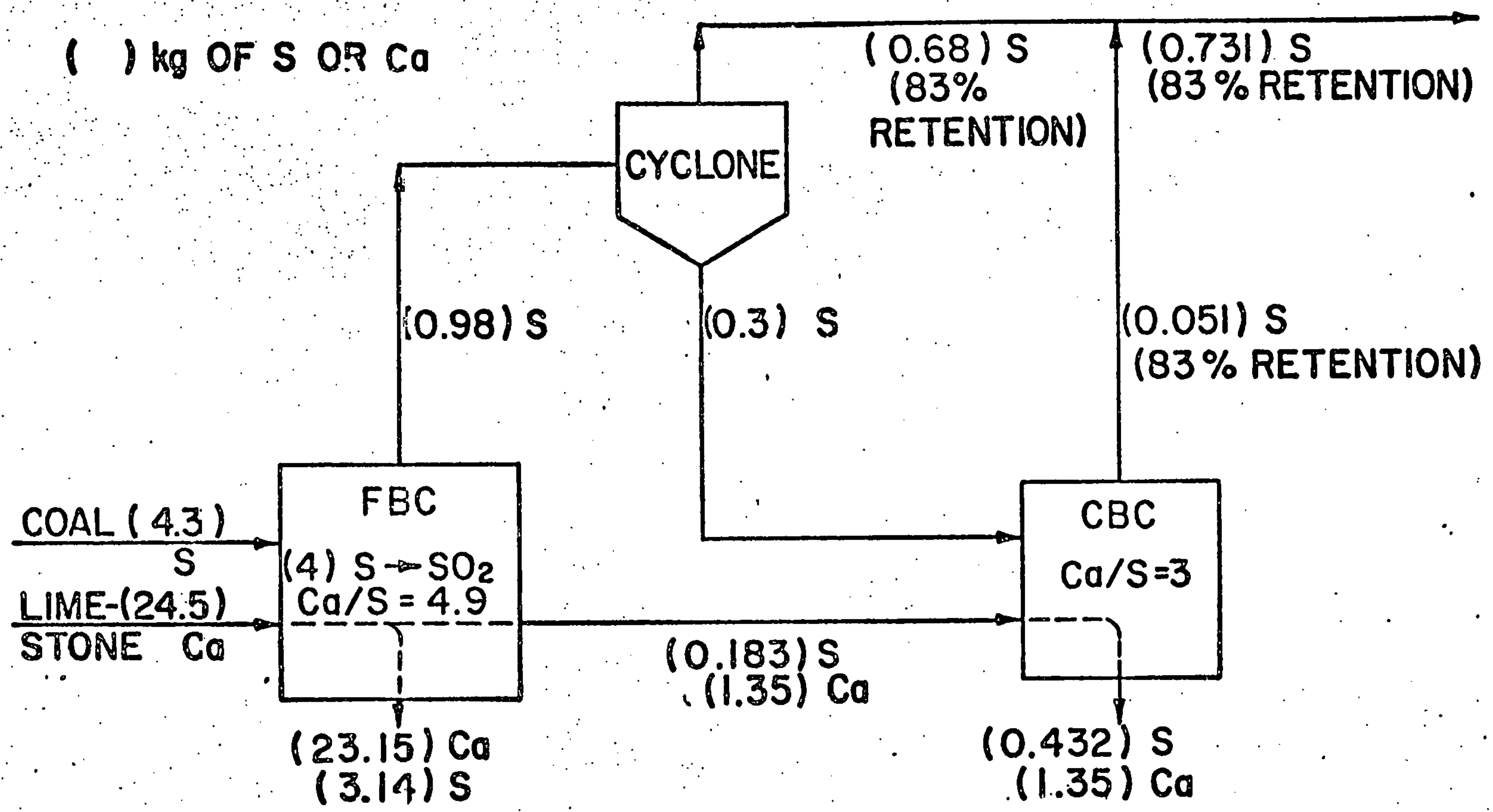

Fig. 4. Sulfur and Calcium Mass Balance for Option 4, using Pittsburg Seam Coal (12,200 Btu/lb), Greer Limestone. Combustor operates at 900°C and 12.5 ft/sec; CBC operates at 1100°C and 6 ft/sec.

cyclone and injected into the CBC. Most likely the elutriated limestone will provide a CaO/S ratio in the CBC in excess of that shown in option 4, (CaO/S of 3)which is needed to obtain 83% SO_2 reduction. If this elutriated limestone had no SO_2 reactivity, the fears of needing a high Ca/S ratio in order to meet EPA SO_2 standards would be realized, thus requiring large amounts of Greer limestone. However, as shown in option 4, this is not the case, the elutriated limestone will have sufficient reactivity to not require excessive limestone quantities. If these projections after pilot plant testing turn out to be low, (due to high elutriation rates in the CBC or other reasons) option 4 suggests that the feeding of combustor bed material (larger particles) or fresh limestone (option 2) to the CBC would be beneficial.

SO_2 REACTIVITY OF OTHER LIMESTONES

The result presented above are only for Greer limestone, which is a highly reactive limestone that has been chosen for use by PER in the 30 MWe demonstration plant. However, limestones have a large variation in SO_2 reactivity that is dependent upon the limestone physical properties. To date, six limestones have been tested, and the trends found are somewhat the same for all calcium-based stones. That is, the qualitive relationship between the SO_2 reactivities of fresh and partially sulfated limestone at 900°C and 1100°C are the same as shown in Fig.1. Thus, for any limestone options 2 and 4 require the least amount of limestone.

Figure 5 compares the SO_2 reactivities of two calcium-based stones with Greer after having been partially sulfated at 900°C (option 4). This figure shows the conversion of available CaO to $CaSO_4$ with time. Tymochtee dolomite has only a somewhat higher reactivity than does Greer.

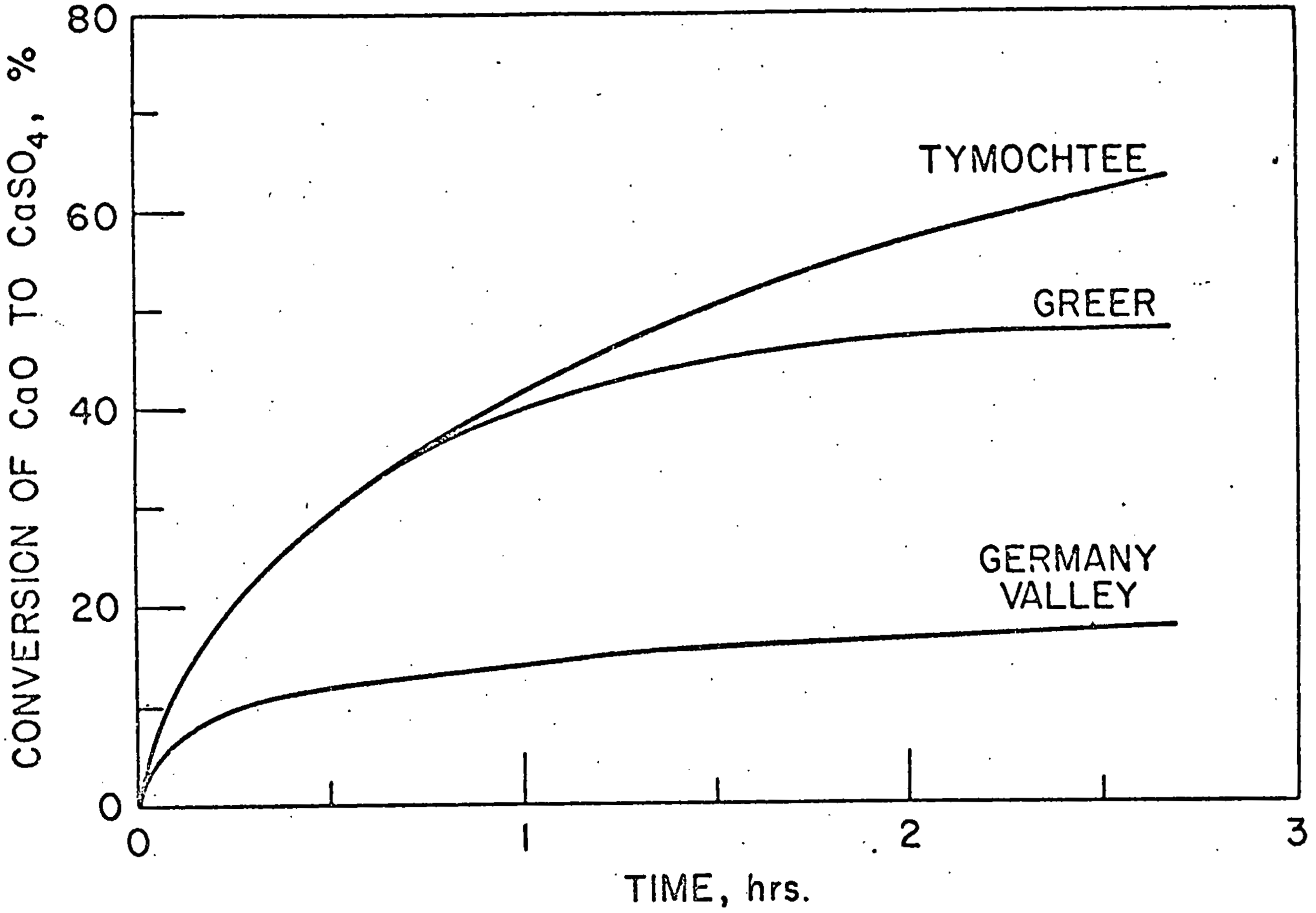

Fig. 5. Reactivity of Partially Sulfated (at 900°C) Limestones with SO_2 at 1100°C. Basis: available CaO.

Germany Valley limestone has a poor reactivity as is typical for high-calcium limestones. However, they all had some ability to react with SO_2, thus some SO_2 retention in the CBC can be expected for any limestone.

The use of high calcium (>95%) limestones, however, may require unexceptably large quantities of limestone for both the combustor and CBC in order to meet the SO_2 standards. Limestone mass feed rates greater than coal may be necessary which would require the strip mining of large areas for limestone and would generate large amounts of solid wastes. This may not be economically or ecologically acceptable.

CONCLUSIONS

The sulfur-removal role of the carbon burnup cell (CBC) in an AFBC system has been analyzed. Four different operating system options are considered. The greatest limestone utilization can be achieved by feeding all of the virgin limestone to the boiler (combustor) and feeding (directly or by elutriation) part of the partially spent limestone from the boiler to the CBC to capture most of the sulfur released in the CBC (option 4). The experimental results suggest that virgin or partially sulfated Greer limestone can be very reactive when fed to the CBC giving the CBC a potentially significant role in reducing SO_2 emissions and meeting EPA standards. Dolomites should perform similar to Greer. High calcium limestones have their greatest SO_2-retention using option 4, however, due to their generally poor SO_2-reactivities, unexceptably large limestone quantities may be required.

Although the results can be quantitatively questioned because the analysis was based on behavior of limestones in an AFBC predicted from TGA experimental data, the predicted trends for the different options are reliable. For example, the predicted overall Ca/S feed ratio for case 1 (Fig. 3) from AFBC experimental data (Fig. 2, curve 1) may be compared with predicted data (Fig. 2, curve 2). The predictions from TGA data project an overall Ca/S of 9.3 which is higher than 4.5 projected with experimental AFBC data. Therefore, it may be expected that the predicted overall Ca/S feed ratios for the four considered options are high estimates.

The differences between the different options definitely confirm that the CBC can play a significant role in reducing SO_2 emission from an AFBC system. Its usefulness can be more fruitfully exploited by adopting option 2 or 4 (Fig. 3).

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