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WORK PLAN FOR CONTINUATION OF THE PROJECT
"REDUCTION OF ATMOSPHERIC POLLUTION BY
THE APPLICATION OF FLUIDIZED-BED COMBUSTION"

by

A. A. Jonke, G. J. Vogel, L. J. Anastasia,
and R. L. Jarry

Work performed under an agreement between the
U.S. Atomic Energy Commission
and the
ENVIRONMENTAL PROTECTION AGENCY
AIR QUALITY OFFICE
DIVISION OF CONTROL SYSTEMS

ARGONNE NATIONAL LABORATORY

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Chemical Engineering Division

April 1971

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ABSTRACT

Additional work is planned on the antipollution aspects of fuel combustion in fluidized beds to which limestone is added. The major emphasis of the next phase of work will be on combustion at pressures up to 10 atm and regeneration of the sulfated lime under pressure. Fluidized-bed combustors will be operated in the one- and two-stage modes to investigate effects on NO_x and sulfur emissions. The program will include laboratory- and bench-scale work aimed at elucidating mechanisms important to sulfur oxide and nitrogen oxide control.

I. INTRODUCTION

This document presents a development program for a continuing study of the lowering and control of the level of pollutants (SO_2 , NO , and particulate) in flue gas from the combustion of fossil fuels, using the fluidized-bed concept. Work at the Chemical Engineering Division of ANL during the past three years has complemented studies of other Air Pollution Control Office (APCO) contractors--British National Coal Board; Esso, Ltd.; Esso, USA; Pope, Evans and Robbins; Consolidation Coal; U. S. Bureau of Mines; and Westinghouse. During research at ANL, the proposed work plan submitted here may be updated and revised to reflect progress made in the technology.

The objectives of the development program at ANL are:

1. To determine how the removal of sulfur oxide (generated during fluidized-bed combustion) is affected by independent fluidized-bed operating variables such as bed temperature, combustor pressure, gas velocity, oxygen concentration, bed height, calcium to sulfur ratio, type of additive and coal, and additive and coal particle size.
2. To determine the effect of operating variables on the level of NO in the flue gas.
3. To compare, as a function of the independent operating variables, the characteristics and quantities of flyash generated in fluidized-bed combustors and in pulverized-fuel boilers.
4. To determine the effects of independent operating variables on the regeneration of CaSO_4 and to investigate various methods of regeneration at elevated pressures.

5. To determine how effectively additive produced by regeneration of CaSO_4 accepts sulfur in the combustor.

6. To determine the chemical and physical mechanisms involved in

a. removal of SO_2 by additive

b. NO formation

c. regeneration of CaSO_4

The justifications for developing methods of lowering the concentrations of noxious pollutants emitted from power- and steam-producing plants are well known. Standards have been set by state and federal governmental agencies for minimum pollutant quantities that may be emitted, reinforcing the urgency of developing an effective process or processes. The program developed by APCO should result in lower pollutant concentrations in the air and, secondarily, may result in a more economical combustion process.

II. PROGRAM HISTORY AND SUMMARY OF FUTURE PROGRAM

ANL studies of the effects of variables in the combustion of fossil fuels at atmospheric pressure were largely made in a 6-in. dia bench-scale combustor. In this work, limestone or dolomite additive was injected into a fluidized bed, where it reacted with sulfur oxide generated by the combustion of coal. The effects of independent operating variables and type of additive on the reduction of SO_2 and NO levels were determined, and these data were supplemented with SO_2 -additive reaction rate data obtained in boat reactor experiments. Coal was the fuel burned in most tests, but in a few, natural gas was combusted to demonstrate the low NO levels achievable and to show that a source of NO formed during coal combustion is nitrogen in the coal. The combustor was operated as a one-stage unit in this work; in one-stage combustion, all of the combustion air is added to the fluidized-bed region, where essentially all combustion takes place. Studies of the effects of variables on SO_2 and NO removal in one-stage combustion are nearly complete, and data on the characteristics and quantities of flyash generated at different operating conditions are being obtained and analyzed.

In another phase of the program, the combustor was operated as a two-stage unit. In two-stage combustion, a substoichiometric volume of air is added to the fluidized bed; the remainder of the combustion air is added to the region above the fluidized bed, where combustion is completed.

The future experimental program at ANL will encompass the following:

1. Completion of study of the effects of variables for one-stage combustion at a pressure of 1 atm. Coal particle size may be the last of the variables to be studied. Additional experiments at 1-atm pressure will be required to aid in establishing the mechanisms involved in pollution control.

2. Determination of the effect of independent variables on SO_2 removal, NO level, and particulate emission, using the atmospheric-pressure

bench-scale combustor in the two-stage mode of operation.

3. Construction of a multipurpose, bench-scale plant for operation at pressures up to 10 atm to study the effects of the most important variables in

- a. one-stage, high-pressure combustion
- b. two-stage, high-pressure combustion
- c. regeneration of the partially sulfated additives from one-stage and two-stage operation

In one-stage combustion, a sulfate is produced that is regenerated to oxide with a reducing gas; in two-stage combustion, a sulfide is produced that is oxidized to regenerate the additive.

4. Continuation of studies to elucidate the mechanisms involved in one-stage and two-stage combustion and the regeneration reactions.

III. PRINCIPAL RESULTS OF ANL FLUIDIZED-BED PROGRAM

To date, studies at ANL using the one-stage fluidized-bed combustion concept and various sets of operating conditions have shown that in the presence of additive,

1. greater than 95% of the SO_2 can be removed from the flue gas,
2. nitric oxide emissions are reduced by 20 to 40% (to <300 ppm) during coal combustion and to the thermodynamic equilibrium limits of ~80 ppm NO during the combustion of natural gas,
3. emission of particulate material of $\leq 5 \mu\text{m}$ diameter is reduced. The emissions from a fluidized bed may be severalfold less than emissions from conventional boiler systems using pulverized coal.

In addition, exploratory experiments using the two-stage combustion concept have shown that

1. a NO concentration of ~70 ppm in the flue gas was achieved,
2. sulfur removal was over 90%.

The bulk of the data have been obtained in one-stage combustion experiments, and the results of these tests and aspects of the problem are discussed below.

A. Sulfur Oxides

1. Sulfur Removal

In the Argonne study of sulfur removal from flue gases during fossil fuel combustion in a 6-in. dia fluidized-bed combustor, coals from Illinois, West Virginia, and Great Britain were used. Additive materials

have consisted of American limestones BCR-1359 and BCR-1360, American dolomites BCR-1337 and Tymochtee, and British limestone. Two types of tests simulating large-scale units operating at steady state have been run in the Argonne 6-in. dia combustor. In the first type of test, an inert fluidized bed of alumina was used with fine particles of additive and essentially all of the additive was elutriated overhead soon after it was fed. In the second type of test, a fluidized bed of large-particle-size additive was used; most of the additive remained in the fluidized bed.

In both types of tests, the most significant variables affecting SO₂ removal were the combustion temperature, the Ca/S mole ratio in the feed streams, and the superficial fluidizing-gas velocity. Less significant variables were the additive type, the coal type, the height of the fluidized bed, the oxygen content of the flue gas, and the particle size of the additive material. Two variables that had no demonstrable effect on SO₂ removals were (1) premixing of coal and additive before they were fed to the combustor (rather than feeding of separate streams) and (2) supplementary heating of the zone above the fluidized bed.

One of the most important variables over the ranges studied is the Ca/S mole ratio in the feed streams. At higher Ca/S ratios, better removals of SO₂ from the flue gas were achieved. Figure 1 shows the effect of Ca/S ratio at 1450-1472°F in runs with two coals and with the same limestone, BCR-1359, in ANL and British combustors. At a Ca/S ratio of 4.2, essentially 100% SO₂ removal was achieved.

The experimental evidence suggests that an optimum temperature exists for each Ca/S mole ratio. For example, for a Ca/S ratio of 4.2, 1450 to 1470°F appears to be the optimum temperature; for a Ca/S ratio of 2.5, the data suggest that the optimum temperature is 1500 to 1550°F. At temperatures above and below the optimum, SO₂ removals are lower.

With increasing superficial gas velocity, SO₂ removal decreases. The decrease is ~5% for a 1 ft/sec increase in velocity.

The less significant variables include fluidized-bed height and oxygen concentration in the flue gas. Increasing the fluidized-bed height from a minimum of 14 in. to a maximum of 48 in. increased the SO₂ removal slightly. SO₂ removals were improved a little by operating to give higher concentrations of oxygen in the flue gas.

The results of the Argonne program show that a fluidized-bed combustor can be operated to reduce SO₂ emissions below the permissible emission levels set by governmental air-pollution agencies. A favorable factor is that sulfur removal is not too sensitive to the types of coal and limestone tested so far in the program. This suggests that it might not be necessary to select specific coals and limestones to achieve low sulfur emission.

2. Mechanism of Sulfur Oxide-Lime Reaction

Ample evidence exists from the ANL work to date that the mechanism of sulfur oxide suppression in the fluidized-bed combustor is much more complex than the simple consecutive reactions involving CaO, SO₂,

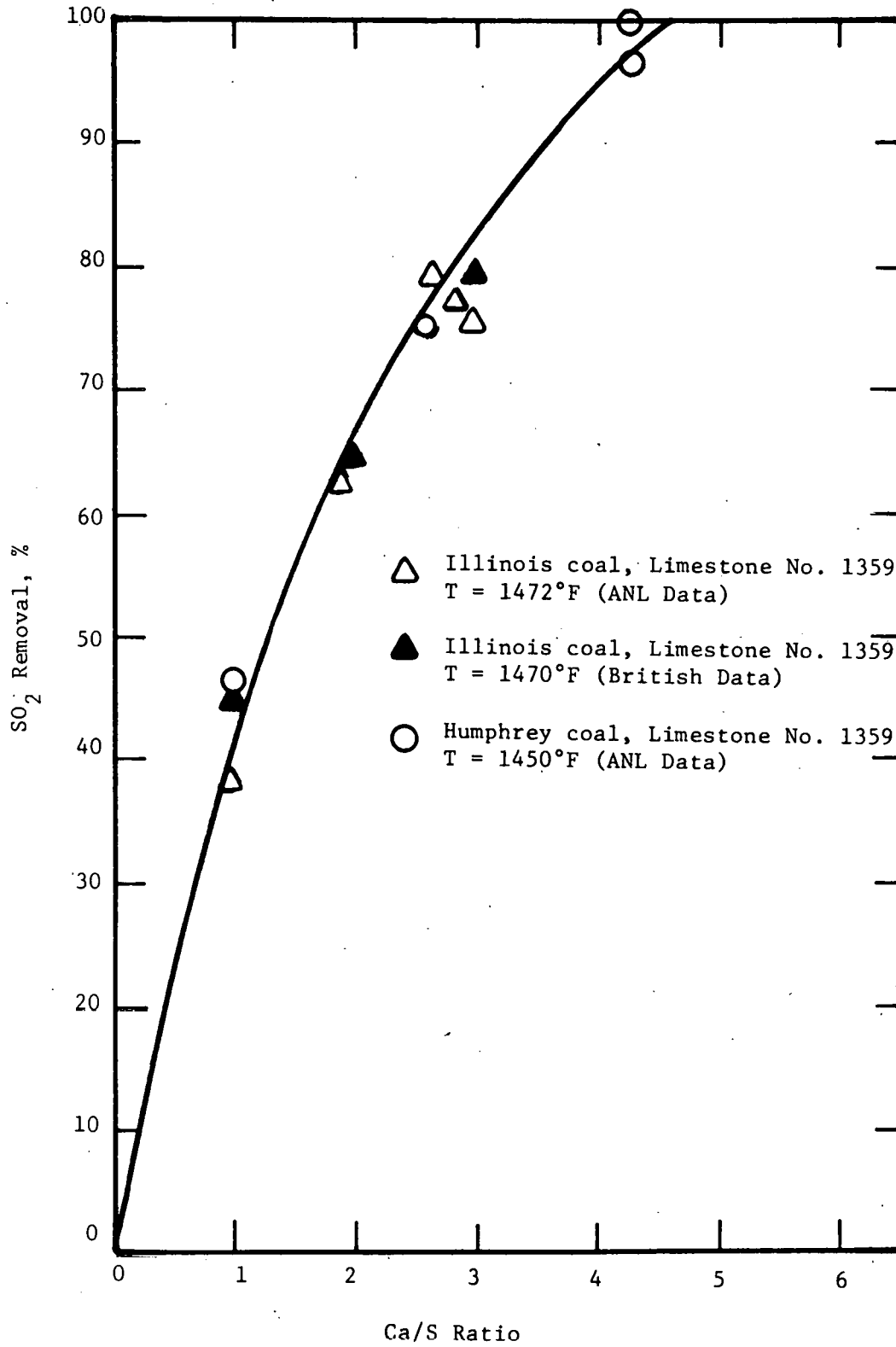
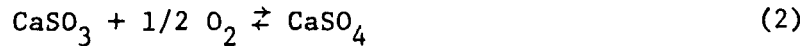


FIG. 1. Effect of Ca/S Ratio on SO₂ Removal for Three Series of Runs (Combustion of two coals in ANL combustor, one coal in British combustor)

and O₂. Many anomalous results have been observed that cannot be explained by the reaction pair,



or the alternative reaction pair,



It is reasonable to suppose that the above reactions do occur in the combustor, but these reactions alone are not sufficient to account for all of the observed results. Some of the evidence that supports a more complex mechanism is the following:

1. ANL work has shown that when a SO₂-air mixture is passed through a bed of calcined limestone at 1500°F, breakthrough of SO₂ occurs much sooner, and lime capacity is much lower, than when the SO₂ is generated in situ by combustion of coal, or when SO₂ is fed to a bed in which combustion of natural gas is occurring. In other words, the efficiency and capacity of a lime bed for SO₂ removal is greater when combustion is occurring than when it is not.

2. ANL examination by electron microprobe of lime particles from the fluidized-bed combustor has shown that sulfur distribution is uniform from the outer surface to the center of many (perhaps most) bed particles. In contrast, a sulfur gradient exists from the surface to the center of coarse lime particles exposed to SO₂-air mixtures; uniform sulfur distribution seems to occur only for particles exposed to reducing flue gases.

3. An optimum temperature range for sulfur suppression of 1450 to 1550°F has been observed in the ANL combustor. This temperature range is appreciably lower than the optimum for SO₂ removal from flue gases outside the combustor (>1600°F). In the fluidized-bed combustor, a rapid decrease in sulfur removal efficiency occurs at temperatures above 1600°F; this is not consistent with most experimental data for the reaction of lime with SO₂ in simulated flue gases.

4. In the fluidized-bed combustor, the optimum temperature for sulfur suppression varies with the Ca/S ratio, being lower at high ratios of Ca/S. The CaO-SO₂-O₂ reaction should exhibit a fixed optimum temperature for a particular type of lime.

5. When natural gas is burned in a partially sulfated bed of lime (without fresh limestone addition), evolution of SO₂ from the bed is observed at temperatures as low as 1650°F; yet decomposition of CaSO₄ is known to occur only at much higher temperatures (>2000°F).

6. When flyash containing partially sulfated lime is recycled to the fluidized-bed combustor, no effect on SO₂ removal is observed; yet this same flyash material is found to have considerable capacity to react with

SO₂ when it is exposed to dilute SO₂-air mixtures.

7. When less than stoichiometric air is fed to the bottom of the combustor and secondary air is fed to the top of the bed, sulfur removal by the lime bed is very poor; yet when the secondary air is fed above the bed, sulfur removal is good.

The above observations suggest that the combustion process itself influences the sulfur oxide reaction with lime. In the fluidized-bed combustor, the sulfur appears to have an exceptional mobility for penetration into lime particles. The observation that SO₂ can be released from the bed at rather low temperatures (1650°F) during combustion of natural gas suggests that chemical reduction of CaSO₄ is occurring despite the introduction of excess air to the bottom of the bed. The need to employ a relatively low temperature (1450-1550°F) for optimum SO₂ retention by the lime bed probably results from the need to minimize the reduction reaction.

a. Mechanism - Macro Effects

Because all the needed information is not yet on hand, our current concept of the mechanism is necessarily speculative. Nevertheless, a description of our current thoughts about the mechanism might help to illustrate its complexity.

It is necessary, first, to consider the flow behavior of gases in the fluidized bed. When air enters the bed at the gas distributor, a portion of the gas flows through the bed in intimate contact with the solids. This is called the "emulsion" phase. The remaining portion of the air flows through the bed in the form of gas bubbles. Continual circulation of gas from the bubbles into the emulsion phase and back into the bubbles takes place as the bubbles rise through the bed. The gas in the bubble phase is available for reaction only as rapidly as it circulates into the emulsion phase. On the basis of combustion efficiency data for the fluid-bed combustor, it is known that circulation of air from the bubbles is essentially completed by the time the bubbles leave the bed. Nevertheless, it is reasonable to assume that in the lower portion of the fluidized bed, circulation of air from the bubble phase has not been completed and that the emulsion phase contains a deficiency of air. Thus the emulsion phase in the lower part of the bed would contain a reducing atmosphere, and the emulsion phase in the upper part of the bed would contain an oxidizing atmosphere.

The behavior of sulfur under the above conditions can be illustrated by an extreme example. In a particular experiment in which the reducing condition in the bed was accentuated by feeding less-than-stoichiometric air at the bottom of the bed, the sulfur concentration in the flue gas was 800 ppm. In another part of the same experiment, when additional secondary air was introduced through a tube in such a way that the air impinged on the top of the bed, the sulfur concentration in the flue gas increased to 3000 ppm. These results suggest that sulfur was accepted by the lime in the lower part of the bed but that reaction with excess air in the upper part of the bed released SO₂. Of course, in a run made under typical single-stage combustion conditions, any such effects would not be as extreme as in this example.

It is well known that CaSO_4 can be reduced rapidly to CaS by reducing gases such as CO or hydrogen at temperatures of about 1750°F . At lower temperatures the rate decreases, and not much is known quantitatively about the kinetics at lower temperatures. The reaction of CaS with air to produce CaO and SO_2 is also well known, but again little is known about the kinetics at the temperatures commonly used in the fluid-bed combustor. It is reasonable to guess that at some combustion temperatures a small portion of the CaSO_4 in the bed can be reconverted to CaO and SO_2 by a mechanism involving circulation of the particles into localized reducing atmospheres resulting from fuel combustion. This is borne out by the experiment in which evolution of SO_2 was observed during combustion of natural gas in a partially sulfated bed at 1650°F . If the oxidation of small amounts of CaS is a part of the mechanism, then some SO_2 may be generated near the top of the bed, limiting the overall sulfur removal.

Thus, it would seem that the reaction in which CaSO_4 is formed from lime and SO_2 is continually being reversed by exposure of the CaSO_4 to localized reducing conditions in the lower portion of the bed. The importance of the reverse reaction would depend upon the conditions in the combustion bed; lower temperatures would minimize the rate of the reverse reaction, high concentrations of reductants would tend to promote the reaction. Thus, the net SO_2 retention could be influenced by combustion conditions and by the distribution of fuel (or the distribution of reducing agents) in the bed. In a large combustor, for example, the number of coal feed points might influence SO_2 removal. Since different coals burn at different rates, the local concentrations of gaseous reductants in the bed may vary from one type of coal to another. Thus, the type of fuel burned may influence sulfur removal, and the optimum combustion temperature may vary slightly for different types of fuel. A number of other factors could be important; for example, in a large combustor with a deep bed that is heavily baffled by steam tubes, the rate of solids circulation would be reduced, thus decreasing the amount of the reverse reaction. Such factors could account for the variability of results achieved in various types and sizes of combustors using various types of coal.

b. Mechanism - Micro Effects

If we conjecture that the circulating bed particles are continually cycling into and out of a reducing atmosphere and that SO_2 can thereby be regenerated from the CaSO_4 , we can now examine the effect this might have on individual additive particles. When a fresh lime (or limestone) particle is fed to the bed, reaction with SO_2 will occur rapidly, forming CaSO_4 , mostly on the outer surfaces and pores of the particle. A condition will soon be reached wherein the probability that an SO_2 molecule will be released from the particle by the reduction mechanism is almost as great as the probability that an SO_2 molecule will be accepted from the bulk gas phase. The particle would then appear to have a low reactivity for SO_2 , although it would still have a considerable capacity for accepting SO_2 at a low rate.

The average residence time of a particle in the fluidized bed is several hours. During this long residence period, the particle

would be subjected to many cycles of alternate reducing and oxidizing conditions. Any SO_2 released by the reduction mechanism would have an opportunity to penetrate deeper into the particle or to escape into the gas phase. Ultimately, a condition would be reached wherein the sulfur is uniformly distributed within the particle at a concentration determined by a pseudoequilibrium set up by the sulfur acceptance and rejection cycle. This sulfur concentration would be appreciably less than that represented by total conversion to CaSO_4 . When this level of sulfur is reached, any additional pickup of SO_2 will be balanced by release of SO_2 so that the sulfur level remains constant.

The above conjectured mechanism would have the effect of limiting the total sulfur pickup by the lime particles. On the other hand, the sulfur would have a greater mobility for penetration into particles, and sulfate shells that would seriously reduce the reactivity and capacity would be avoided. Preliminary experimental data indicate that the net effect is a greater reactivity and capacity for SO_2 removal by fluidized lime beds in which combustion is occurring than in similar beds in which combustion is not occurring.

Let us now consider the fine lime particles contained in recycled flyash. These particles, which are only lightly converted to sulfate, have considerable capacity for accepting additional SO_2 as is observed when they are exposed to SO_2 -containing gases. Yet when the flyash is recycled to the combustor, there is little apparent effect on SO_2 removal. This could be explained by assuming that the outer sulfate-bearing portion of the particles is already in sulfur-equilibrium with the fluidized-bed combustion medium. With the very short residence time of these particles in the fluidized bed, any further sulfur penetration into the particle is insignificant. Thus, the recycled particles pass through the bed with little apparent change.

Next considered is the feeding (to a coarse-particle bed) of coal and limestone at rates corresponding to very high ratios of lime to sulfur. As the Ca/S ratio is increased, the average residence time of the additive particles decreases proportionately. At high Ca/S ratios, the probability that an SO_2 molecule will be picked up near the outer surface of a relatively fresh particle rather than penetrating into an aged particle increases. Thus, at high Ca/S ratios, a sulfur gradient within a particle is more likely. Under these circumstances, the relative effect of the "reverse" reaction (reduction of CaSO_4) becomes greater, and the temperature for optimum SO_2 removal would be slightly lower. This hypothesis conforms to the experimental evidence that the optimum combustion temperature is lower at a Ca/S ratio of four (1450°F) than at a Ca/S ratio of two (1550°F).

c. Significance to the Process

The above-proposed mechanism needs to be verified or disproved by experimental work. Chemical kinetics experiments and the use of the electron microprobe to determine sulfur distributions in particles will be important tools for this work.

The ANL program is attempting to establish the details of the complex physical-chemical reaction mechanism that determines the sulfur-control capabilities of the fluidized-bed combustion process. Unless a better insight into the mechanism is gained, it will be extremely difficult to extend experimental data to scaled-up facilities or to conditions that are different from those used in the experiments. Unfortunately, the mechanism involved appears to be intimately associated with the fluid dynamic behavior of the fluidized bed, and so cannot be elucidated by chemical studies alone. Nevertheless, a better understanding of the chemistry would be very helpful toward understanding the mechanism.

Regardless of whether the precise details of the mechanism as now visualized are correct, there can be little doubt that the mechanism is not a simple one. If sulfur removal is indeed influenced by the combustion conditions, then fluctuations or intentional changes in the operating conditions of a plant-scale combustor could have important influences on sulfur emission. Moreover, one cannot assume that the use of increasing excesses of lime (high Ca/S ratios) will compensate for other factors, since there is evidence to show that changes in Ca/S ratio need to be accompanied by other changes. The use of empirical methods alone does not seem adequate for establishing the sulfur-control capabilities of fluidized-bed combustion.

B. Nitrogen Oxides

1. NO_x in Flue Gases

Nitric oxide (NO) is formed during the combustion of coal and is an important contributor to air pollution. In coal combustion experiments, nitric oxide levels of 300 to 800 ppm have been measured in the presence of ~3 vol % oxygen in the flue gas. At this oxygen concentration and at the combustion temperatures used, a thermodynamic equilibrium concentration of only 80 ppm NO is expected as a result of nitrogen fixation. The results of several Argonne experiments showed that the source of the NO emitted during the combustion of coal is the nitrogenous content of the coal itself (1 to 1.5 wt % in U.S. coals).

The presence of limestone or dolomite in the fluidized bed during the combustion of coal results in NO emission being reduced by about 10 to 40%. Although the mechanism for this reduction in NO level is not known, possibly decomposition of NO by catalysis is promoted in the presence of CaO and/or CaSO₄.

Experimental data gathered during the Argonne study do not correlate the operating variables strongly with nitric oxide emissions. Apparently, the type of coal and the Ca/S mole ratio are the most significant variables; with higher Ca/S ratios, NO emissions are slightly higher. The West Virginia and British coals apparently emit more nitric oxide than does the Illinois coal. The reasons for this, however, are not clear; regression analyses of the data are continuing. A relationship between NO emission and a physical or chemical property of the coal may be found for correlating the experimental results.

Exploratory work at ANL has shown that when less than stoichiometric air is fed to the fluidized bed and secondary excess air is fed above the bed, the NO level in the flue gas corresponds to the equilibrium value for nitrogen fixation (~70 ppm). Apparently, under reducing conditions the nitrogenous compounds in the coal are not converted to NO.

2. Mechanism

Nitrogen oxides (essentially all NO) in the flue gas of fluid-bed combustors are mainly produced from the nitrogenous content of the coal. The concentrations observed in the flue gas are generally many times greater than is predicted from the equilibrium for the nitrogen fixation reaction. Therefore, control of the nitric oxide via this route is not indicated. Other methods such as chemical reduction or catalytically enhanced decomposition seem indicated.

Nitric oxide content of the flue gas from fluid-bed combustors has been studied by several investigative teams.¹ At all of these installations, it was observed that the NO concentration in the flue gas tended to decrease upon the addition of limestone. Recently, British workers observed an increase in the NO concentration with dolomite addition and SO₂ reduction in a pressurized combustor.² In other reported work,³ the NO concentration was observed to decrease with an increase in SO₂ concentration at atmospheric pressure; these workers speculate that an interaction between NO and SO₂ is responsible for the lowering in NO level.

a. Decomposition

A mechanism for the control of NO in the flue gas is decomposition:



This reaction, though favorable according to the equilibrium, is apparently not fast enough to reduce the chemically generated NO to the equilibrium value of less than 100 ppm at 1600°F. Limited use of catalysts as decomposition promoters has not been successful.

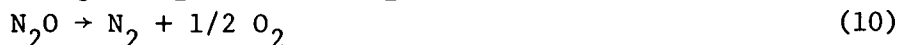
In the case of pressurized combustors in which the bed depth can be relatively large, the greater residence time of the NO in the bed after formation might result in greater decomposition. It is also possible that elevated pressures may affect the formation of NO. The behavior of NO under pressurized combustion conditions needs further study.

b. Chemical Interaction

Another mechanism for the control of NO in the flue gas is chemical interaction. Two reactions between components of the fluid-bed system have been proposed to account for the lowering of NO content. One is



In this reaction, any reduction in SO₂ concentration in the flue gas (by reaction with limestone) could shift the reaction to the left, thereby diminishing the NO concentration. Measurement at ANL of NO₂ levels in the flue gas did not confirm this hypothesis. An alternative proposed pathway for NO reduction is a series of reactions involving CaSO₃ and a complex with NO:



This decomposition mechanism has not been proved.

c. Reducing Conditions

Two-stage combustion represents one of the most promising methods for control of NO emissions in fluidized-bed combustion. Apparently, the absence of excess oxygen in the combustion bed prevents the oxidation of nitrogen compounds in coal. A small amount of NO is produced above the bed by fixation of nitrogen.

C. Particulate Matter

Particulate matter emitted from fluidized beds consists of flyash and unburned carbon from the combustion of coal and fine particles of additive material (which are either part of the additive feed or are decrepitated from larger additive particles during fluidization). In the Argonne fluidized-bed system, particulate matter is removed from the flue gas by two cyclone separators in series and a final dust filter.

Carbon in the particulate matter represents the largest loss of unburnt carbon from the system. In the Argonne combustor, about 80 to 90% of the unburnt carbon loss occurs by elutriation of fine particles in the exhaust gases before combustion is complete; the remaining 10 to 20% of the carbon loss is due to the formation of CO and C_xH_y in the flue gases. Overall combustion efficiencies of 93 to 97% have been demonstrated with coal in the fluidized-bed unit without flyash recycle. Combustion efficiencies can be increased by recycling the elutriated solids to the fluidized bed or to a carbon burnup cell.

In all experiments at Argonne, a relatively small coal particle size of -12 mesh (~1/16 in. or less) has been used, and all of the flyash has elutriated from the fluidized bed. In the 6-in. dia combustor, the maximum coal size has been limited by the necessity of air-transporting the coal through small lines.

1. Additive Carryover

Since the elutriated matter is a mixture of solids of different origins and compositions, the fraction of additive carryover due to decrepitation and attrition of bed material can only be estimated as part

of the total carryover. For example, all of the flyash and additive particles having diameters less than 177 μm are expected to elutriate from the fluidized bed at superficial gas velocities of 2.6 ft/sec. In an experiment of 39-hr duration, the amount of calcium collected in the overhead solids corresponded to only slightly more than the total weight of minus 177- μm particles fed. Thus, it was calculated that less than two percent of the larger limestone (BCR-1359) particles had decrepitated. In other experiments, the data indicate that carryover of BCR-1359 limestone can be as high as 9% of the total additive and fluidized-bed inventory. In single experiments, the carryover of BCR-1360 limestone was approximately 20% and that for dolomite BCR-1337 was approximately 85% (this high carryover was estimated from both the calcium and the magnesium material balances for BCR-1337).

The results indicate that decrepitation of BCR-1359 limestone is small and that use of this type of additive material in a full-scale fluidized-bed combustor with regeneration and recycle of additive should be possible. In comparison, more limestone BCR-1360 and dolomite BCR-1337 (stones containing MgCO_3) appeared to be carried over in a single use of the additive than was observed for BCR-1359. The effect of regeneration-recycling on decrepitation of these materials needs to be determined.

2. Particle Size of Elutriated Fines

The particle size distribution of elutriated fines was determined in early experiments at Argonne (ANL/ES/CEN-1001, p. 32); these analyses showed that less than 4% of the particles passing into the cyclone separators had a diameter of $\leq 8 \mu\text{m}$. Even though the cyclones selected for the experimental equipment may not be optimum in size or design, the collection efficiency for the combined cyclones has ranged from 95 to 99%. This efficiency range places the particulate carryover beyond the secondary cyclone as low as 0.1 gr/ft³, which is much less than the projected particulate emissions (0.5 gr/ft³) from power generation plants at a 1970 control level of 87% removal.⁴

Since a pressurized fluidized-bed boiler could easily handle coal crushed to a top size of 1/8-in. dia, smaller quantities of flyash of $\leq 5\text{-}\mu\text{m}$ dia would be generated in a pressurized unit than in a conventional coal-fired plant in which coal pulverized to very fine particles is used. Thus, emissions of particles of $\leq 5\text{-}\mu\text{m}$ diameter might realistically be⁵ expected to be severalfold less than emissions from conventional plants⁵ burning pulverized coal.

IV. PLANS FOR FUTURE WORK

A. One-Stage Combustion Experiments at One-Atmosphere Pressure

1. Experimental Work

The continuation of the experimental program of one-stage, atmospheric-pressure combustion will be aimed chiefly at the elucidation of the sulfur-removal mechanism and the study of certain variables that

may be of particular importance. The Westinghouse concepts for design of fluidized-bed combustors propose relatively high gas velocities (>6 ft/sec) and, in the case of the pressurized combustor, relatively high temperatures (1750°F). ANL work has shown that high gas velocities are detrimental to SO₂ removal. To be determined is whether this effect can be overcome by increasing the Ca/S ratio or by other means.

Several additional experiments will be needed that are specifically aimed at studying the sulfur-removal mechanism. For example, combustion of coal in a bed of anhydrite (CaSO₄) might be expected to release SO₂, if the proposed mechanism discussed in Section III.A.2 above is correct. These experiments will be designed as further information is gathered.

Several experiments will be needed to verify that the optimum temperature for SO₂ removal is a function of Ca/S ratio. Some experiments at higher Ca/S ratios than heretofore employed will be needed to determine whether SO₂ removal continues to increase or remains constant above a certain Ca/S ratio.

Most of the important independent operating variables have already been evaluated. A small amount of work is still needed to examine the effect of coal particle size, a potentially important variable. In addition, demonstration runs could be made with fuels such as char, lignite, oil shale, and residual oil, but this work will be given a low priority.

2. Correlation of Results

The correlation of experimental results is currently under way by two methods, regression analysis and modelling studies. The objective of regression analysis is to obtain a mathematical expression for predicting the expected reduction in SO₂ emission as a function of the significant independent variables, which are the bed temperature, Ca/S ratio, and gas velocity. A similar equation is being developed for NO level in the flue gas. These correlations are being updated as additional experimental results are obtained.

In the second correlating method, a mathematical model is derived for the combustion of coal in a fluidized bed with the release of sulfur and its capture by the additive. Actual data and predicted data are compared. Currently, results from either modelling or regression analysis predict SO₂ removals with a standard error of ~8%. However, both methods, at the current stage of development, assume that the types of coal and additive used do not affect SO₂ removal, which is not true. Additional refinement of the correlations should allow predictions with lower standard error. Further development of the mathematical model will depend on the availability of time and manpower.

3. Topical Report

A topical report will be prepared on the results of fluidized-bed combustion work done at ANL after all experimental work at 1-atm pressure has been completed.

B. Pressurized Combustion

1. Background Information

Capital costs of a fluidized-bed combustor operated at high pressures (~ 10 atm) may be lower than those for a fluidized-bed combustor operated at atmospheric pressure.⁶ Westinghouse cost studies project a capital cost decrease of $\sim 20\%$ for a pressurized combustor and $\sim 6\%$ for an atmospheric fluidized-bed combustor in comparison to a pulverized-fuel plant. BCURA estimates tend to confirm these cost projections.⁷ Additionally, in the case of pressurized combustion, the practicability of combining gas and steam cycles (recovering energy from the combustion gases by use of a gas turbine) may lead to an improvement of 2 to 5% in power generation efficiency.⁸

The decreased volume required for a pressurized combustor promises to decrease the capital cost for construction in comparison to a unit operated at atmospheric pressure. At a given superficial gas velocity, the quantity of heat generated in a unit operated at 10-atm pressure will be ten times that for an atmospheric combustion unit having the same cross-sectional area. Alternatively, a pressurized unit operated at 10 atm would require only one-tenth the cross-sectional area of an atmospheric unit to produce a given quantity of heat. Additional savings may result from shop fabrication rather than field erection.

2. Design of ANL Experimental Pressurized Combustion System

A bench-scale pressurized combustor-regenerator will be constructed that will be used for regeneration studies in addition to 10-atm combustion studies. No sulfur recovery system will be installed. The components will be similar to those of the atmospheric combustion unit, but operable at 10 atm. The major components will be the combustor-regenerator, solids feeding system, and particulate removal system. Preliminary design information for the combustor-regenerator indicates that the material of construction should be type 316 stainless steel⁹ and that the pressurized-shell approach should be followed. The unit will probably be 8 in. in diameter, and a 1-in. thick shell of refractory material will be installed on the wall for the regeneration studies. In the combustion step, the projected overall heat-transfer coefficient is expected to be ~ 75 Btu/(hr)(ft²)(°F). Projected heat generation rate per unit volume of fluidized bed will be limited^{10,11} to $\sim 450,000$ Btu/(hr)(ft³), and the required heat transfer surface^{10,11} will be ~ 8 ft²/ft³ of bed. In detailed design studies, the following items must be considered:

- a. Heat transfer surface availability and orientation
- b. Gas and solids distribution and mixing
- c. Solids feed preparation (the possibility of premixing coal and additive)
- d. Prevention of overpressurization
- e. Automatic solids-withdrawal systems
- f. Feed system for alternative fuels such as gas and oil

3. Experimental Program

The experimental work will be designed to systematically study the variables affecting SO_2 , NO_x , and particulate emissions during combustion of coal at 10-atm pressure and to provide insight on reaction mechanisms. Regeneration and reuse of the additive material will also be an important part of the pressurized-combustion study. Reaction of SO_2 with additive and regeneration of additive will be done in close conjunction; the products of one operation will be the starting material for the other.

a. Laboratory-Scale Work

Laboratory-scale equipment that has been constructed from a 2-in. dia, schedule 80, type 316 stainless steel pipe will be used to study the reaction of SO_2 with limestone and dolomite at 10-atm pressure. A synthesized mixture of flue gas constituents at various concentrations will be passed through a fixed bed of dolomite or limestone. The experimental program will provide preliminary information on the effects of temperature, pressure, and gas composition on SO_2 removal and NO level. A total of eight variables (limestone or dolomite additive, pressure, temperature, concentrations of O_2 , H_2O , NO , and CO/CH_4 in the inlet gas, and precalcination of stone) are being considered in a 2^{8-4} fractional factorial experiment. Variables showing a significant effect can be evaluated further.

b. Bench-Scale Experiments

The variables determined to be significant in bench-scale experiments at atmospheric pressure and in laboratory-scale experiments at 10-atm pressure will be incorporated into the study of bench-scale fluidized-bed combustion at 10-atm pressure. Experiments will be focused on maximizing SO_2 removal with several additives and several coals. The effects of these variables on NO_x emissions will be observed. Preliminary BCURA results for pressurized fluidized-bed combustion have shown low NO_x concentration in the flue gas and also an increase in NO_x concentration when SO_2 emission was reduced by the injection of dolomite.¹²

Particulate entrainment will also be determined, since higher entrainment rates¹³ may be encountered under pressurized operation. Since combustion at 10-atm pressure will allow an appreciable pressure drop across the cyclone separators, particulate removal is expected to be good with inexpensive mechanical separators. Also, since elutriated additive particles mixed with flyash probably will not be reusable, decrepitation of regenerated and recycled additive will be determined as a function of regeneration conditions and number of cycles.

The effects of regenerated and reused additive on SO_2 , NO_x , and particulate emissions will be evaluated. The number of additive reuse cycles feasible, the additive SO_2 sorption capacity as a function of number of cycles, and the requirements for fresh additive will have important effects on the commercial feasibility of the process.

Pressurized combustion of other fuels such as oil, gas, coal char, and lignite may also be studied later in the investigation.

4. Material and Energy Balances

In conjunction with the development program, material and energy balances will be required so that realistic engineering appraisals can be made with regard to process economics and scale-up. Such work will be done only as a guide to the development program, and will not overlap or duplicate work done in the Westinghouse part of the overall program.

Figures 2 and 3 are illustrative schematic flowsheets for one-stage and two-stage fluidized-bed combustion and additive regeneration.

C. Two-Stage Combustion

Fossil fuels can be burned to carbon dioxide and water in either one- or two-stage combustors. In one-stage combustion, the fossil fuel is burned within a fluidized bed of solids consisting of partially sulfated lime. Air in excess of the stoichiometric requirement is used, typically about 15% excess.

In contrast, in two-stage combustion, less than the stoichiometric volume of air (e.g., 50-80% of stoichiometric) required for complete combustion is added to the fluidized bed of lime (the first stage). Relatively large volumes of carbon monoxide and hydrocarbons are produced, and these are burned to carbon dioxide and water by adding excess air to the gas in a second stage. This second stage can be the region above the fluidized bed in the same combustor or can be a separate reactor. In one-stage combustion, little carbon is present in the fluidized bed; in two-stage combustion, a relatively large inventory of carbon is present. A char can be produced if a very low percentage of the stoichiometric combustion air is added to the first stage. Not included in this investigation will be study of a char-producing process (in which a char must be removed continuously if a constant bed level is to be maintained).

1. Advantages of Two-Stage Combustion

Two-stage combustion has several potential advantages over one-stage combustion. A high gas temperature can be maintained in the second stage, where the carbon monoxide and hydrocarbons are burned, and the temperature in the first stage can be maintained in the 1400-1550°F range to maximize the reaction of CaO with sulfur compounds generated during combustion. If the gas leaving the second stage of the combustor is at a high temperature and in addition the combustor is operated at high pressure (for example, 10 atm), the second-stage gas can be routed to a gas turbine for direct conversion of the energy to power. Thus the overall process efficiency can be higher than in the conventional process in which the combustion gas is routed to a steam-producing heat exchanger and the raised steam is used to drive a turbine. Another advantage is that less heat would be released in the first or fluidized-bed stage of a two-stage combustor and less water-steam tubing would be required in the bed. Also, the velocity of the gas passing through the fluidized bed would be lower than in one-stage combustion or, alternatively, the bed area could be smaller.

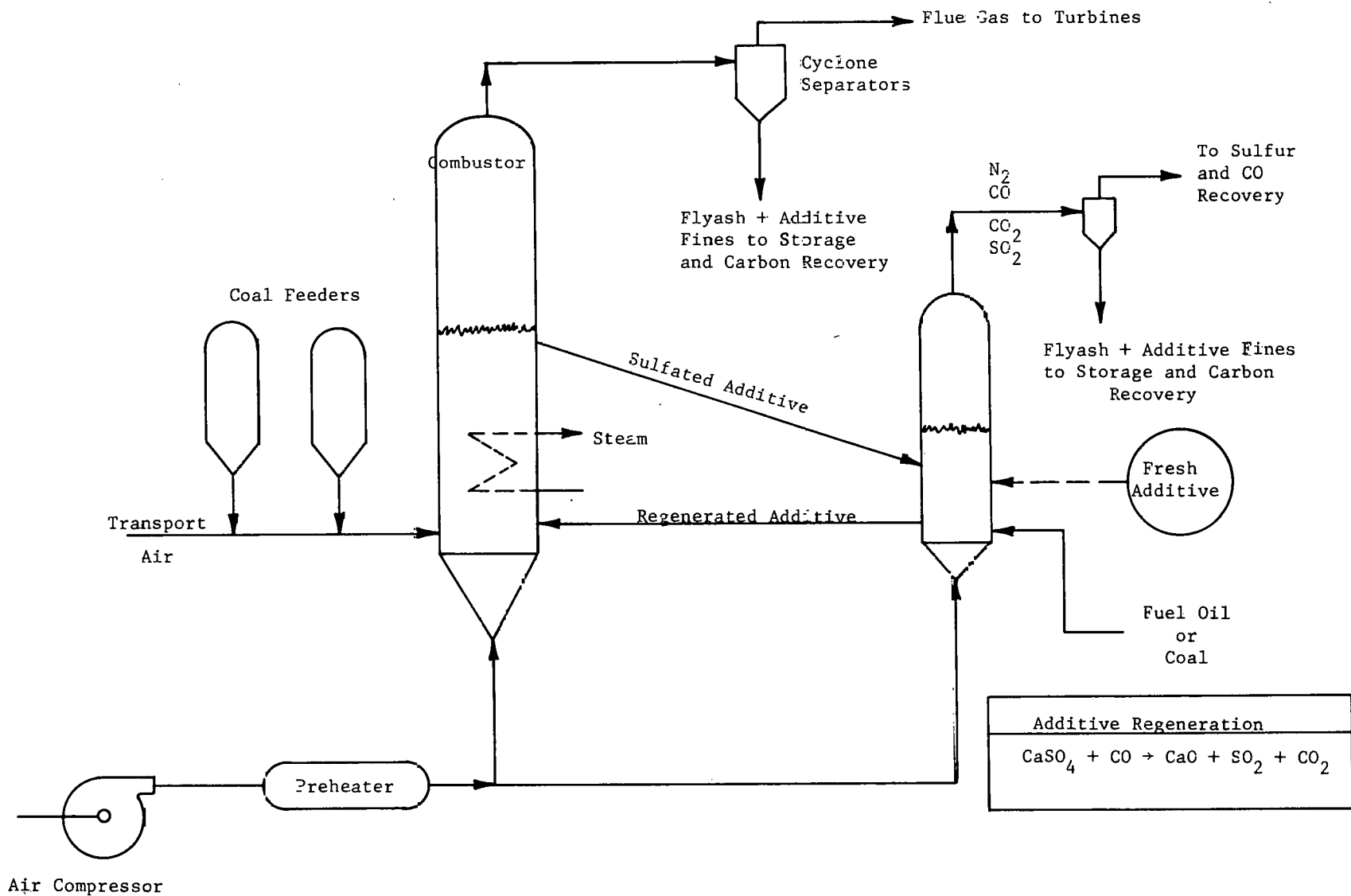


FIG. 2. One-stage Fluidized-bed Combustion with Regeneration of Additive

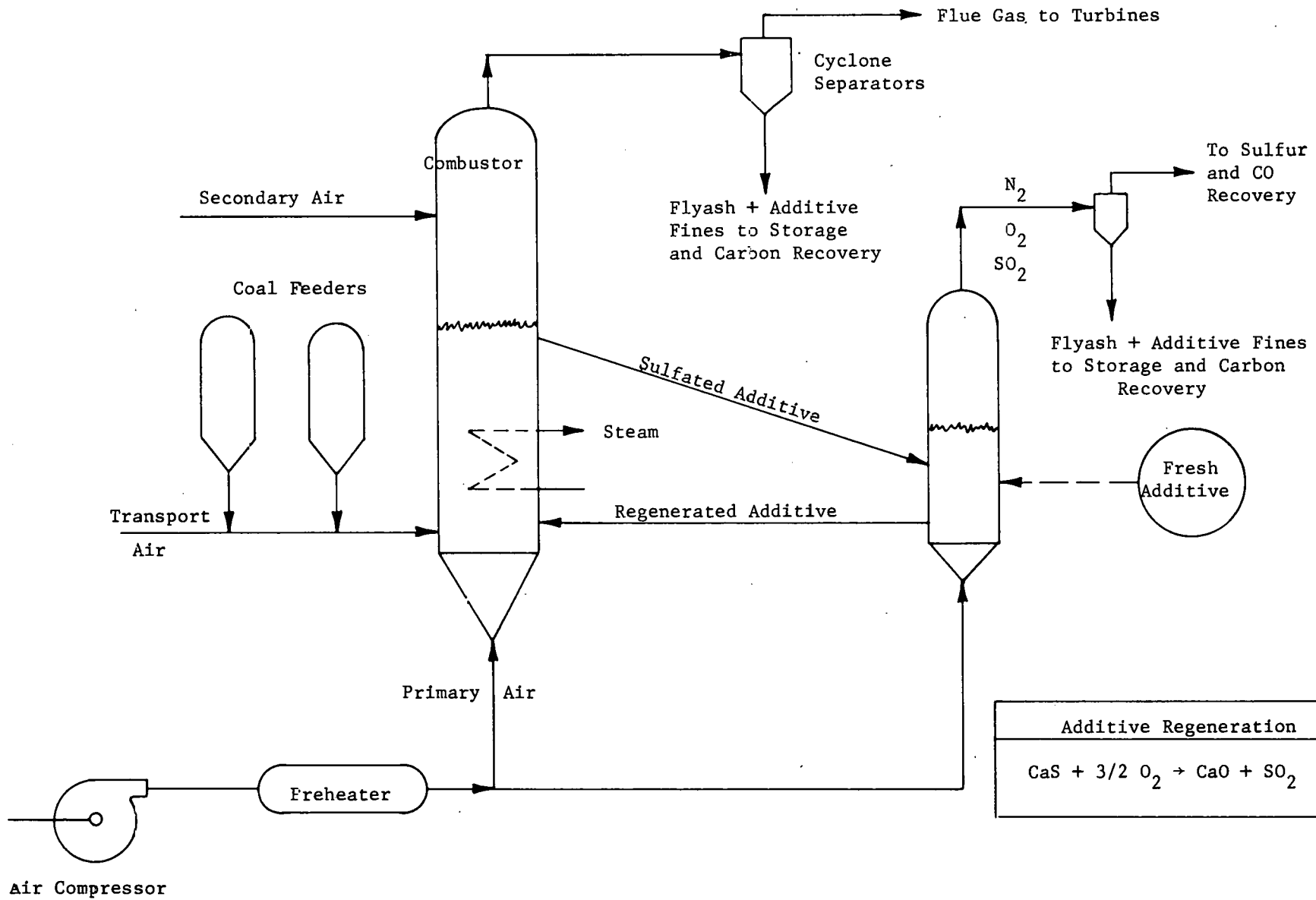


FIG. 3. Two-stage Fluidized-bed Combustion with Regeneration of Additive

Another potential advantage of two-stage combustion is that the lime-sulfur product may be in the form of CaS rather than CaSO₄. The regeneration of CaS can be accomplished readily by oxidation with air, consumes no reducing agent, and is not affected by pressure.

Most importantly, NO concentrations in the flue gas would be low. In four exploratory, two-stage coal combustion experiments made in the ANL 6-in. dia combustor, the NO concentration in the flue gas was as low as 70 ppm (ANL/ES/CEN-F026), considerably lower than the 250-550 ppm NO concentrations obtained in one-stage experiments. Also, greater than 90% of the sulfur was reacted with lime. Under optimum conditions, sulfur removal will probably be as high as in the one-stage combustion experiments--96-98%.

2. Experimental Program

Before two-stage combustion experiments are started aimed at determining the effects of independent variables on SO₂ and NO concentrations in the flue gas, the available literature will be searched for equilibrium and thermodynamic data for the reactions involved and for results obtained in similar processes. The Babcock-Atlantique "Ignifluid" (two-stage, fluid-bed process) has been developed to a relatively large 60-MW scale.¹⁴ However, although the combustion concept has been demonstrated, little or no information is available on the concentrations of NO and sulfur that can be expected in the flue gas if limestone or dolomite is injected into the fluidized bed to reduce these emissions. The British two-stage oil-combustion studies should provide some information on pollutant concentrations in the flue gas and on removal of pollutants by regenerated lime.¹⁵ However, these data would be for oil combustion only and would be for a relatively narrow set of conditions.

Some information on NO and sulfur levels should be available from studies of processes that produce a burnable gas (gasifiers), such as processes being developed by the Institute of Gas Technology, Bituminous Coal Research, Inc. and Consolidation Coal.¹⁶ With the exception of the Consolidation Coal process, in which sulfur is removed by calcined dolomite, no information will be available on pollutant levels in the flue gas in the presence of additive. Some corrosion information should be available from these gasification process studies, and this would aid in the design of a two-stage combustor.

Initial experiments will be designed to explore the practicality of the concept in comparison with the one-stage combustion concept. These experiments will examine the minimum amount of air deficiency (below stoichiometric) that can be employed in the first stage (fluidized bed) without appreciable NO_x formation. This information may be important in evaluating the potential corrosion of tubes in the bed under reducing conditions. The initial experiments will also attempt to determine whether the second combustion stage can readily achieve high combustion efficiency without re-formation of SO₂ above the bed.

After this phase of the work is completed, a decision will be made, in conjunction with APCO, as to whether further work should be done

toward optimizing the process. If the two-stage studies are continued, the next phase of the program will not be specified until a literature review is completed and the effects of variables in one-stage combustion studies are reviewed. Probably, the effects of some independent variables will be small, limiting the number of experiments needed in the two-stage combustion studies. The independent variables include the first-stage temperature, the first-stage air addition rate (also represented by gas velocity), the calcium to sulfur ratio in the feed streams, the coal and additive particle sizes, the second-stage temperature, the second-stage excess-air addition rate (also represented by gas velocity), and the gas pressure inside the combustor. Dependent variables include the concentrations of sulfur oxide, NO, and reducing gases in the gas stream leaving the first stage and the second stage, the concentration of coal char in the bed, the overall combustion efficiency, and the rate of particulate emission from the combustor. An additional independent variable that can be tested is the type or source of coal and limestone (although one-stage combustion experiments at ANL have indicated that coal source may have a relatively small effect on SO₂ removal).

The initial testing will be at atmospheric pressure using the existing ANL combustor. This will be followed by runs in the pressurized combustor. The major purpose of the atmospheric-pressure experiments will be to acquire information to evaluate two-stage operation, thus aiding in decisions on overall program direction.

In all of these experiments, the bed particles will be analyzed chemically and with an electron microprobe for CaS and CaSO₄ concentrations and distributions at the different levels of air stoichiometry used in the tests. Substoichiometric air levels that result in good removals of SO₂ and low levels of NO with good operability of equipment will be recommended for larger scale studies.

Corrosion information will be obtained by metallurgical examination of (1) corrosion coupons, (2) combustor components at the end of the experiments, and (3) failed equipment, if any.

D. Regeneration of Limestone Materials

Since efficient SO₂ removal in coal combustion will require that relatively large quantities of limestone be used, it will be desirable to regenerate the partially sulfated limestone for recycle and to recover the sulfur value as sulfuric acid or elemental sulfur.

The justification for regeneration and reuse of the limestone material is reduction of the waste burden imposed by the sulfur-removal process. U.S. coals contain about 10 wt % ash, which is elutriated out of the combustor in the flue gas and must be removed before the flue gas is vented to the atmosphere. Presently, only a small fraction of this ash is utilized - about 20%, mainly in the manufacture of concrete aggregate and concrete blocks. The use of limestone for SO₂ removal would increase the waste burden by many times. For example, for a 4 wt % S coal and with a calcium to sulfur (Ca/S) ratio of 1 in the feed streams, about 10 lb of limestone would be added for the combustion of 100 lb of

coal. Therefore, the total waste burden per ton of 4 wt % S coal consumed at a Ca/S stoichiometric ratio of 4, assuming no regeneration and reuse of the limestone, would be as high as 1000 lb. The use of a dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) instead of limestone would double the contribution of the sulfur-removal process to the waste burden. Although a byproduct market might be found for this material, this cannot be assumed.

Regeneration and reuse of the limestone material is therefore a desirable process step. An integral regenerator is suggested. A regeneration system operated at 10 atm is favored because of the ease of coupling it to a 10-atm combustor and for reasons of economy of size for a given throughput of material. However, if high SO_2 levels in the regenerator off-gas cannot be obtained at 10 atm, operation at a lower pressure may be required.

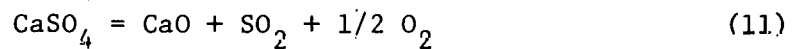
1. Literature Review

A comprehensive literature review and evaluation will be made as part of the program to select a process or processes for study of cycles in which partially sulfated limestone is regenerated and sulfur is recovered from the CaSO_4 or CaS formed during coal combustion. The regeneration process involves reduction of CaSO_4 or oxidation of CaS, depending on whether combustion is done under oxidizing or reducing conditions.

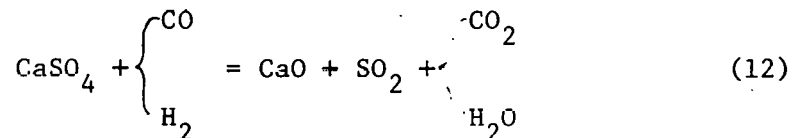
The following preliminary literature survey is intended mainly to indicate the possible scope of the investigations and to serve as a basis for additional information gathering. It consists almost exclusively of material from HEW and OCR contractors. Included is work at Consolidation Coal on several processes¹⁷⁻²⁰ for regenerating partially sulfated limestone and recovering sulfur from CaSO_4 or CaS formed in the fluidized-bed combustion of fossil fuel.

The major reactions considered for use in a regeneration cycle are the following:

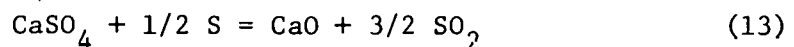
Dissociation of CaSO_4



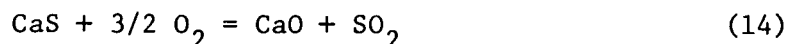
Reduction of CaSO_4 by CO or H_2



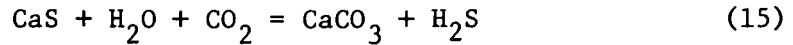
Reduction of CaSO_4 by Sulfur Vapor



Oxidation of CaS



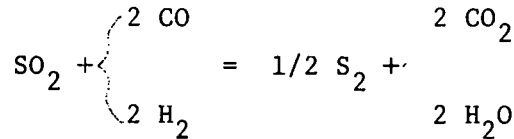
Reaction of CaS with H₂O + CO₂



The temperatures required for these processes are quite varied; reaction 11 requires temperatures of 2200°F or greater, reactions 12, 13, and 14 can be accomplished at about 1900-2000°F, and reaction 15 is reported to proceed satisfactorily at 1000°F at elevated pressures.

Reactions 11, 13, 14, and 15 are relatively straightforward with relatively simple equilibrium relationships. Reaction 12, however, is complicated by intermediate reactions and is affected in a rather complex manner by the CO/CO₂ ratio in the gas stream. The intermediate reactions for reaction 12 are considered in some detail in subsection b below.

Sulfur can be recovered from SO₂ produced in the regeneration step by subsequent reduction of SO₂ with either CO or H₂ as shown below.



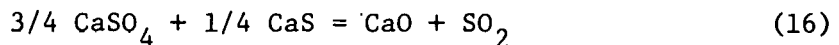
a. Dissociation of CaSO₄

Thermodynamic and equilibrium data for the dissociation reaction are available in several reports.²¹⁻²³ An experimental investigation of the kinetics of the dissociation reaction was performed by workers at Muscle Shoals Facility of TVA.²⁴ Both the equilibrium data and the kinetic data indicate that temperatures of ~2400°F would be required to achieve a satisfactory rate of dissociation of CaSO₄. For example, if a temperature of 2500°F and a P_{O₂} of 0.03 atm are assumed, the P_{SO₂} would be almost 0.06 atm, giving an SO₂ concentration in the effluent of 26 vol %.

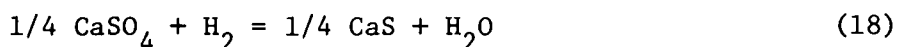
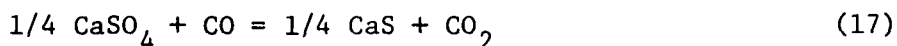
Operation of a regenerator at 2500°F would probably not be feasible due to material of construction limitations. If the temperature were reduced to 2000°F, still rather high from the material of construction standpoint, the SO₂ concentration predicted by the equilibrium data is 2 x 10⁻³ vol %, which is far too low for an economic process.

b. Reduction of CaSO₄ by CO or H₂

Overall reactions of partially sulfated limestone with carbon monoxide¹⁸ or hydrogen at high temperatures (ca 1900°F) are given above as reaction 12. The intermediate reaction whereby SO₂ gas is actually removed is



The CaS for reaction 16 is formed as follows:

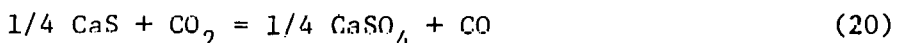
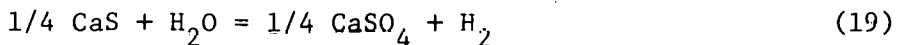


Of the reactions pertaining to this regeneration cycle, reactions 12 and 16 are desirable but reactions 17 and 18, which convert CaSO_4 only to CaS and consume large quantities of reductants, should be allowed to occur only to the extent needed to provide CaS for reaction 16. Reactions 12 and 16 are favored at high temperatures and reactions 17 and 18 at lower temperatures. High SO_2 release should be obtainable by reaction 12 with high CO/CO_2 and $\text{H}_2/\text{H}_2\text{O}$ ratios, but these conditions also favor reactions 17 and 18, which produce CaS but do not release SO_2 . The equilibrium constant values for reactions 17 and 18 depend on the fourth power of the CO/CO_2 and $\text{H}_2/\text{H}_2\text{O}$ ratios. A CO/CO_2 ratio of 1/2 (in the inlet gas stream) was found to produce mostly CaO and SO_2 in preference to CaS at most temperatures.²³

A reaction temperature greater than 1880°F but no greater than 2060°F is needed for regeneration with CO or H_2 . For example, operation at 2060°F and 1 atm with a 10% CO -20% CO_2 mixture resulted in $\sim 8\%$ SO_2 in the exit-gas stream, and operation with a 15% CO -30% CO_2 mixture resulted in $\sim 11\%$ SO_2 in the exit gas stream. In both cases, 95% of the CaSO_4 was converted to CaO and the remaining 5% was converted to CaS .

c. Regeneration by the CaSO_4 - CaS Reaction

As noted above, CaO and SO_2 may be produced by a solid-solid reaction of CaS with CaSO_4 (equation 16). If the product of the sulfur-fixation reaction is CaS , the CaSO_4 needed for reaction 16 can be formed by the following reactions:



The regeneration step of a gasification process developed by Consolidation Coal^{17,20} (CO_2 acceptor process in which the sulfur is fixed as CaS) consists of a solid-solid reaction between CaSO_4 and CaS in a regenerator to produce CaO and SO_2 . In tests at 315 psia, the SO_2 concentration in the effluent gas stream from the regenerator was about 0.23 vol %.

For the case in which CaSO_4 rather than CaS is the starting sulfur-containing material, the overall process consists of conversion of a portion of the CaSO_4 to CaS as shown in equation 17, followed by the solid-solid reaction (reaction 16). For CaSO_4 and CaS to coexist as a result of reaction 17, the CO_2/CO ratio in the exit gas needs to be near the equilibrium ratio of 46.²² Bench-scale experiments were performed in which the CO_2/CO ratio was in the range 23-30 (richer in CO than the equilibrium ratio), and 93% or more of the sulfur was removed from the solids.

d. Reduction of CaSO₄ by Sulfur Vapor

We have learned indirectly about a study carried out in a European country on the reduction of CaSO₄ with elementary sulfur in a fluidized bed. A mixture of air and sulfur vapor was used at temperatures of 1800-2000°F (reaction 13). The objective of the work was to evaluate the possibility of using the mineral, anhydrite, as a source of sulfur for sulfuric acid production. A cost comparison with conventional processes was made.

The results and details of this work are not available at present, but further information will be sought.

e. Oxidation of CaS

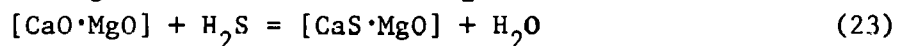
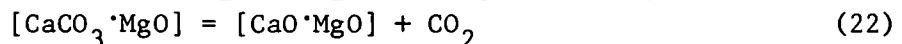
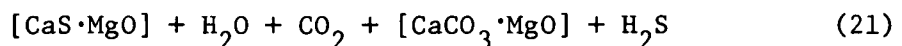
A procedure for regeneration of sulfided lime (produced during combustion at partially reducing conditions) requires temperatures in excess of 1900°F and oxidizing conditions.¹⁵ The overall reaction, performed at 1900-1950°F, is given in equation 14 above. As in the other proposed sulfur-removal procedures, solid-solid reaction of CaSO₄ with CaS is also involved in this scheme, the CaSO₄ being produced by oxidation of a portion of the CaS.

A mode of effecting regeneration of CaS that has been tested experimentally is to interrupt fuel addition to a gasifying fluid bed and continue operation with air alone. Exothermic reaction 14 raises the bed temperature substantially, producing SO₂. For a continuously operating regenerator, the temperature would be controlled at a selected air input rate by controlling the circulation rate of the bed material.

The life of fluid-bed material for this combination of gasifying-regeneration has been tested in experiments consisting of as many as 60 cycles.¹⁵ The conclusions reached were as follows: (1) 100% desulfurizing capacity can be obtained indefinitely at a makeup rate of 1.5 wt CaO per wt sulfur, (2) when particle size changes from 810 μm to 635 μm, the absorption-desorption is not affected, and (3) at makeup rates of about 1.5 wt CaO per wt sulfur, the desulfurizing efficiency is stabilized in less than 10 cycles.

f. Regeneration of Partially Sulfated Dolomite with H₂O + CO₂

Processes have been described for regeneration of dolomite that has taken up sulfur under reducing conditions²⁵ and under oxidizing conditions.²⁶ For the former case, the feed to the regenerator is CaS·MgO, and regeneration is carried out using water vapor and CO₂. The complete cycle, with operating conditions of 1000°F and 220 psi, is outlined in the following reactions:



Heat evolved by reaction 21 is said to be sufficient to raise steam or to superheat steam. Reaction 22 would be best performed at a temperature just below the equilibrium decomposition temperature of CaCO_3 at the prevailing CO_2 concentration.

The regeneration of $[\text{CaSO}_4 \cdot \text{MgO}]$ to produce $[\text{CaCO}_3 \cdot \text{MgO}]$ has also been studied;²⁶ the kinetics are favorable at temperatures as low as 1100°F . Half-calcined dolomite is the expected product from partial calcination in a pressurized combustor.

Regeneration of material produced under oxidizing conditions, $[\text{CaSO}_4 \cdot \text{MgO}]$, differs in only one step (the initial step) from the regeneration scheme outlined in equations 21 to 23. In the initial step, sulfate is reduced to sulfide at about 1470°F , using hydrogen as shown in equation 18.

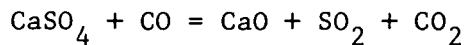
2. Technical Evaluation of Candidate Processes

A complete technical evaluation of candidate processes will be made as part of the program. The following is a preliminary evaluation.

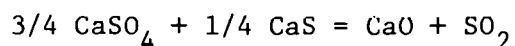
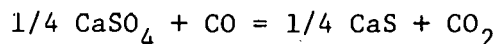
Current information on regeneration of limestone material used for removing sulfur during the combustion of fossil fuels indicates that regeneration processes may operate at temperatures as high as $\sim 2000^\circ\text{F}$ or as low as 1100°F , depending upon the method used. Both sulfated limestone (CaSO_4) and sulfided limestone (CaS) can be processed. By a proper choice of reaction conditions and reactant concentrations, the concentrations of SO_2 or H_2S in the effluent gas phase can be sufficiently high to allow sulfur recovery as either dilute H_2SO_4 or as elemental sulfur.

The lower-temperature processes for regeneration of a dolomite proposed by Squires, $<1400^\circ\text{F}$, appear attractive because they can be conducted under pressure and because the temperature is low. However, if the material to be regenerated is CaSO_4 rather than CaS , an extra step is needed. These processes need further evaluation.

An example of an experimental study of a promising regeneration process for partially sulfated limestone from a coal combustor operated in the oxidizing mode has been described.¹⁸ In this regeneration operation, the overall reaction (reaction 12) is the following:



However, the actual chemistry involves two consecutive reactions:



In work at Consolidation Coal, excess CO was combusted to furnish heat for the overall endothermic process, which has a heat of reaction of 59.2 kcal/mole. The compositions of input and output gas and solids streams are shown diagrammatically in Fig. 4 for the first of six sulfation-regeneration cycles.¹⁸ The gas compositions are given in vol % on a dry basis. In the sixth cycle, the regeneration step was still removing 94% of the sulfur content of the sulfated dolomite. Although dolomites have proved suitable for multicycle use, Esso R&E²³ found that limestone No. 1359 has high attrition-resisting qualities.

The CO₂/CO ratio of 30 (in the exit gas) for the regeneration cycle depicted above is desirable to maximize sulfur removal from the solids. The equilibrium value at 1950°F is reported by Consolidation Coal to be 46. With a lower CO concentration and therefore a higher CO₂/CO ratio, less sulfur is removed.

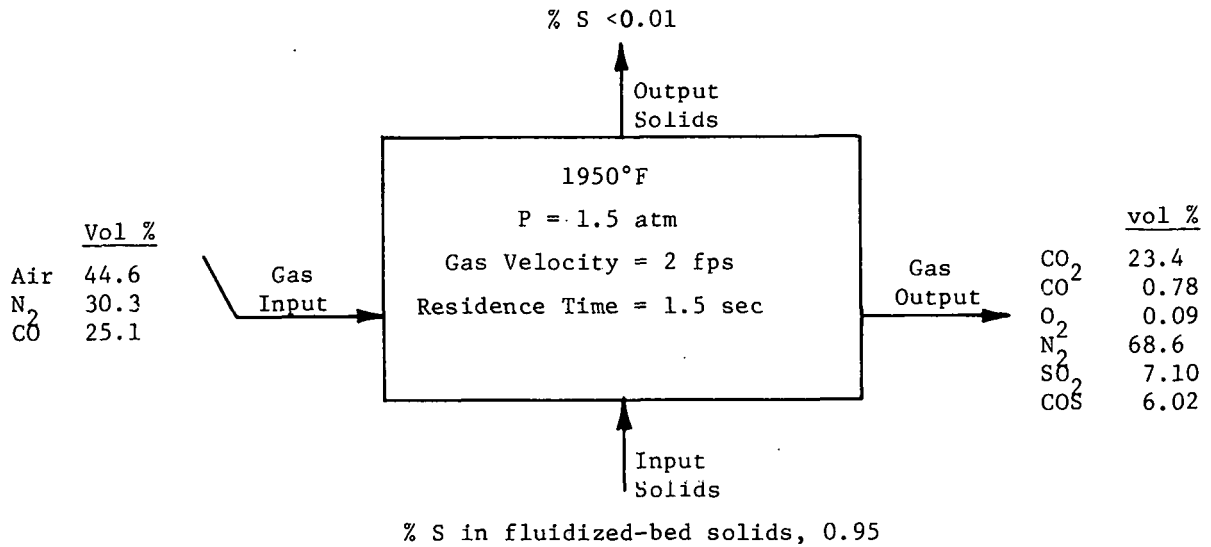


Fig. 4. Sulfation-Regeneration Cycle for Partially Sulfated Limestone

3. Pressure Effects in Regeneration

An important variable in a regeneration process is the total pressure of the system. Since a high-pressure process is envisioned, the effect of pressure - especially on the concentration of SO_2 in the gas phase - must be evaluated. In general, the effect of pressure on the equilibrium is to compensate in the manner predicted by the LeChatelier principle of mobile equilibrium. The principle states that the equilibrium system will shift in such a manner as to minimize the effect of a change in temperature or pressure. Therefore, an increase in the pressure of the total system (not an increase in the pressure of a gas component that does not react) will cause the equilibrium to shift to the side having fewer gaseous molecules. The reverse is true for a decrease in the pressure of the total system. Increasing the fraction of a nonreacting gas component in an equilibrium system does not change the equilibrium point, i.e., the relationship between the various reacting gaseous components remains the same.

Candidate regeneration reactions are listed in Table 1. Also listed in Table 1 are the equilibrium relationships, free energies, ΔG_R , and the change in the number of gaseous molecules, Δv , if the reaction proceeds at 2000°F as written. These data show that the principal reduction reactions of CaSO_4 (Table 1, equations 2 and 3) would be affected unfavorably by an increase in the system pressure; the oxidation reactions of CaS (Table 1, equations 7, 9, and 10) would be favored by an increase in the system pressure. With respect to reactions 2 and 3, although the SO_2 concentration for a certain volume throughput of reducing agent would be reduced by increasing the system pressure, this might be offset by increasing the concentration of reducing agent. Thus, for example, increasing the CO/CO_2 ratio in the exit gas would increase the SO_2 concentration in that gas but would increase the CO requirements. To compensate for the increased CO requirement, the exit gas (after sulfur removal) might be cycled to the combustor to consume the CO .

From this brief review, it is apparent that a systematic examination of the effect of pressure on selected regeneration systems should be made. Calculation, probably by an iterative computer program, of the equilibrium concentrations of the gaseous components as a function of both temperature and pressure will be necessary in the evaluation of regeneration processes and the selection of reaction conditions that will maximize the SO_2 concentration in the gas phase.

4. Experimental Program

The experimental program will comprise both laboratory-scale and bench-scale studies.

a. Laboratory-Scale Studies

In the laboratory-scale studies, the initial emphasis will be on screening candidate regeneration processes, followed by evaluation of reaction parameters for guidance of the bench-scale work.

TABLE 1. Equilibrium and Thermodynamic Functions
for Reactions of Interest for Regeneration^a

No.	Reaction	Kp =	Kp	Δv	ΔG _R
1	$\text{CaSO}_4 \rightleftharpoons \text{CaO} + \text{SO}_2 + 1/2 \text{O}_2$	$\frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{1}, \text{ atm}^{3/2}$	1.54×10^{-5}	+1.5	30.10
2	$\text{CaSO}_4 + \text{CO} \rightleftharpoons \text{CaO} + \text{SO}_2 + \text{CO}_2$	$\frac{P_{\text{SO}_2} P_{\text{CO}_2}}{P_{\text{CO}}}, \text{ atm}$	28.7	+1	-9.11
3	$\text{CaSO}_4 + \text{H}_2 \rightleftharpoons \text{CaO} + \text{SO}_2 + \text{H}_2\text{O}$	$\frac{P_{\text{SO}_2} P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}, \text{ atm}$	57.8	+1	-11.02
4	$1/4 \text{CaSO}_4 + \text{CO} \rightleftharpoons 1/4 \text{CaS} + \text{CO}_2$	$\frac{P_{\text{CO}_2}}{P_{\text{CO}}}$	53.3	0	-10.80
5	$1/4 \text{CaSO}_4 + \text{H}_2 \rightleftharpoons 1/4 \text{CaS} + \text{H}_2\text{O}$	$\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$	107	0	-12.71
6	$3/4 \text{CaSO}_4 + 1/4 \text{CaS} \rightleftharpoons \text{CaO} + \text{SO}_2$	$P_{\text{SO}_2}, \text{ atm}$	0.537	+1	1.69
7	$\text{CaS} + 3/2 \text{O}_2 \rightleftharpoons \text{CaO} + \text{SO}_2$	$\frac{P_{\text{SO}_2}}{P_{\text{O}_2}^{3/2}}, \text{ atm}^{-1/2}$	2.21×10^{14}	-1/2	-89.70
8	$\text{CaSO}_3 \rightleftharpoons \text{CaO} + \text{SO}_2$	$P_{\text{SO}_2}, \text{ atm}$	2.47	+1	-2.46
9	$\text{CaS} + 2 \text{O}_2 \rightleftharpoons \text{CaSO}_4$	$\frac{1}{P_{\text{O}_2}^2}, \text{ atm}^{-2}$	1.48×10^{18}	-2	-113.63
10	$\text{CaS} + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{S}$	$\frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2\text{O}} P_{\text{CO}_2}}, \text{ atm}^{-1}$	3.63×10^{-4}	-1	21.52

^aAll data apply to 2000°F; ΔG_R is in kilocalories mole⁻¹.

The experimental equipment that will be utilized in the laboratory-scale work is an already constructed all-stainless steel system consisting of two 2-in. dia vertical tube reactors and associated manifolding and gas handling and supply arrangements. This system is shown schematically in Fig. 5. Although the system was designed for fixed-bed experiments, it can be modified for fluidized-bed operation by the addition of suitable solids-filtering equipment. The system can be operated at 150 psig and up to 1800°F.

Screening experiments will be performed at 10-atm pressure to select the reductant and process chemical concentrations necessary to produce a high enough volume fraction SO₂ in the exit gas for sulfur-recovery processes. A gas phase concentration of about 10 vol % is considered adequate for recovery as sulfuric acid or as elemental sulfur.

In the second phase of the laboratory-scale program, the effect on the regeneration reaction of variation in reaction parameters such as temperature, reagent concentration, gas flow rates, and solid feed sulfur concentration will be investigated. In addition, the composition of output gas and solid streams will be studied. From this work, reaction conditions will be set for bench-scale experimentation.

b. Bench-Scale Program

The bench-scale program will utilize the fluidized-bed reactor now being designed for operation at 10-atm pressure. A single reactor will be used for both combustion and regeneration work. Experiments will be performed using the range of process parameters established in the laboratory-scale work. This work will include the following items but will not necessarily be restricted to them.

1. Investigate reaction rates for regeneration as a function of operating temperature, inlet gas composition, and other variables.
2. Specify the compositions of input and output solids and gaseous process streams.
3. Demonstrate limestone makeup, recycle, and attrition rates.
4. Demonstrate reactivity of regenerated limestone.
5. Investigate sulfur recovery processes if this is found to be necessary on the basis of the literature search.

On the foundation of prior bench-scale and laboratory-scale work, a demonstration of sufficient operation time and number of recycles will be made to achieve operating data and experience.

c. Literature Survey and Evaluation

Simultaneously with setting up of the experimental program, the literature will be searched on topics of interest for limestone regeneration. Both the contractor literature and open literature will be

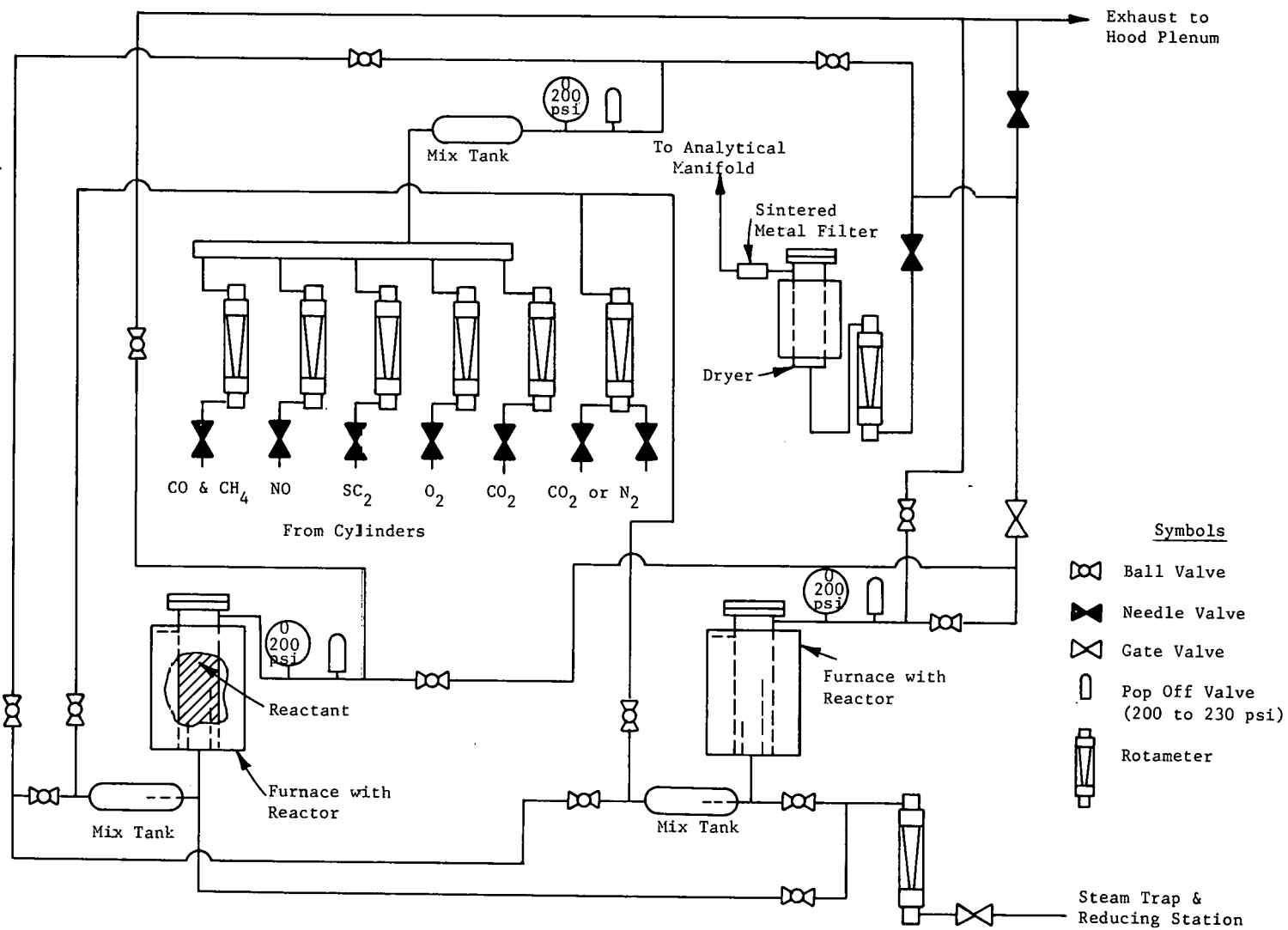


FIG. 5. Laboratory-Scale Reactors and Associated Equipment

surveyed and critically analyzed. Not only will potential regeneration systems be listed as a guide in the selection of the process, but also thermodynamic and kinetic data will be collated.

E. Kinetics, Equilibria, and Mechanisms

This part of the ANL program will involve experimental and theoretical studies applied to both the combustion and the regeneration processes. The fundamental problems being considered are the following.

1. Experimental Studies

a. Mechanism of the Sulfation Reaction

The apparent complexity of the sulfation mechanism and the importance of understanding the mechanism were discussed in an earlier part of this document. In order to elucidate the mechanism, it is planned to utilize the following approaches:

1. Electron microprobe examination of individual particles will be used to determine the distribution of sulfur under various operating conditions. For example, in order to establish whether combustion conditions affect the manner in which sulfur distributes within lime particles, the electron probe will be used to compare sulfur distribution in particles from runs in which combustion is occurring with sulfur distribution in runs in which combustion is not occurring. Similarly, comparisons can be made for runs performed under a variety of combustion conditions.

2. The kinetics of pertinent reactions, such as the reactions of carbon monoxide with CaSO_4 , will be studied at combustion temperatures to determine whether the reaction is sufficiently energetic at these temperatures to explain the apparent "regeneration" or reversal of the CaSO_4 formation reaction. These experiments will be conducted on a laboratory scale in a fixed-bed reactor.

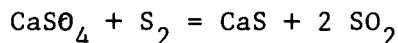
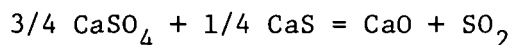
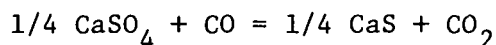
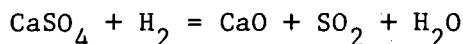
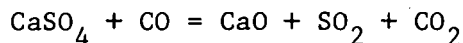
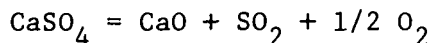
3. Specific experiments will be designed for the bench-scale fluidized-bed combustor to provide insight into the mechanism or to provide bed material for electron microprobe examination. An example of a possible experiment would be to carry out a combustion run with a pure CaSO_4 bed (without limestone addition) to determine whether SO_2 is evolved under these conditions.

b. Characteristics of Flyash

The characteristics and composition of flyash particles may be important from the standpoint of their potential effect on gas turbine blades, problems of fine particle emissions, ash sintering problems in carbon burnup cells, etc. The electron microprobe, together with optical microscopes, will be useful in establishing the characteristics and elemental composition of particles, as well as investigating the process of agglomeration of particles. Such work will be carried out as the need becomes apparent.

2. Literature and Thermodynamic Surveys

Results of bench-scale combustor experiments suggest that a physical or chemical process is operating to limit the ultimate reduction in SO_2 concentration in the flue gas. Reactions involving the sulfation product CaSO_4 , in which reducing reactions would be involved, seem to be likely candidates for such limiting steps. Therefore, the literature should be thoroughly scanned and the thermodynamics examined for reactions such as those listed below.



Another possibility is that the reduction in SO_2 concentration in the flue gas might be limited by reactions in which CaO is removed by combination with other constituents in the fluid-bed system, such as Fe_2O_3 , Al_2O_3 , and SiO_2 . Calcium ferrite ($\text{CaO}\cdot\text{Fe}_2\text{O}_3$) can be formed at the temperatures employed in fluid-bed combustors.

The extent or completeness of combustion in the fluidized bed seems to influence the sulfation reaction of lime. Techniques for complete combustion of the carbon in a fluidized-bed combustor will be reviewed. A thorough review of the mechanism and kinetics of the carbon combustion reaction, in particular the $\text{CO} + 1/2 \text{O}_2 = \text{CO}_2$ reaction, might indicate a means of ensuring more complete combustion.

The effect, if any, on SO_2 removal of the type of coal and the quantity and types of sulfur present in the coal will be reviewed. Correlation of the results of fluid-bed combustor experiments with the sulfur content and the physical and chemical properties of the coals used is of interest.

The possible relationship of a temperature effect (SO_2 removal optimized at a specific temperature) to changes in reaction mechanism or stoichiometric conditions of the sulfation reaction will be reviewed.

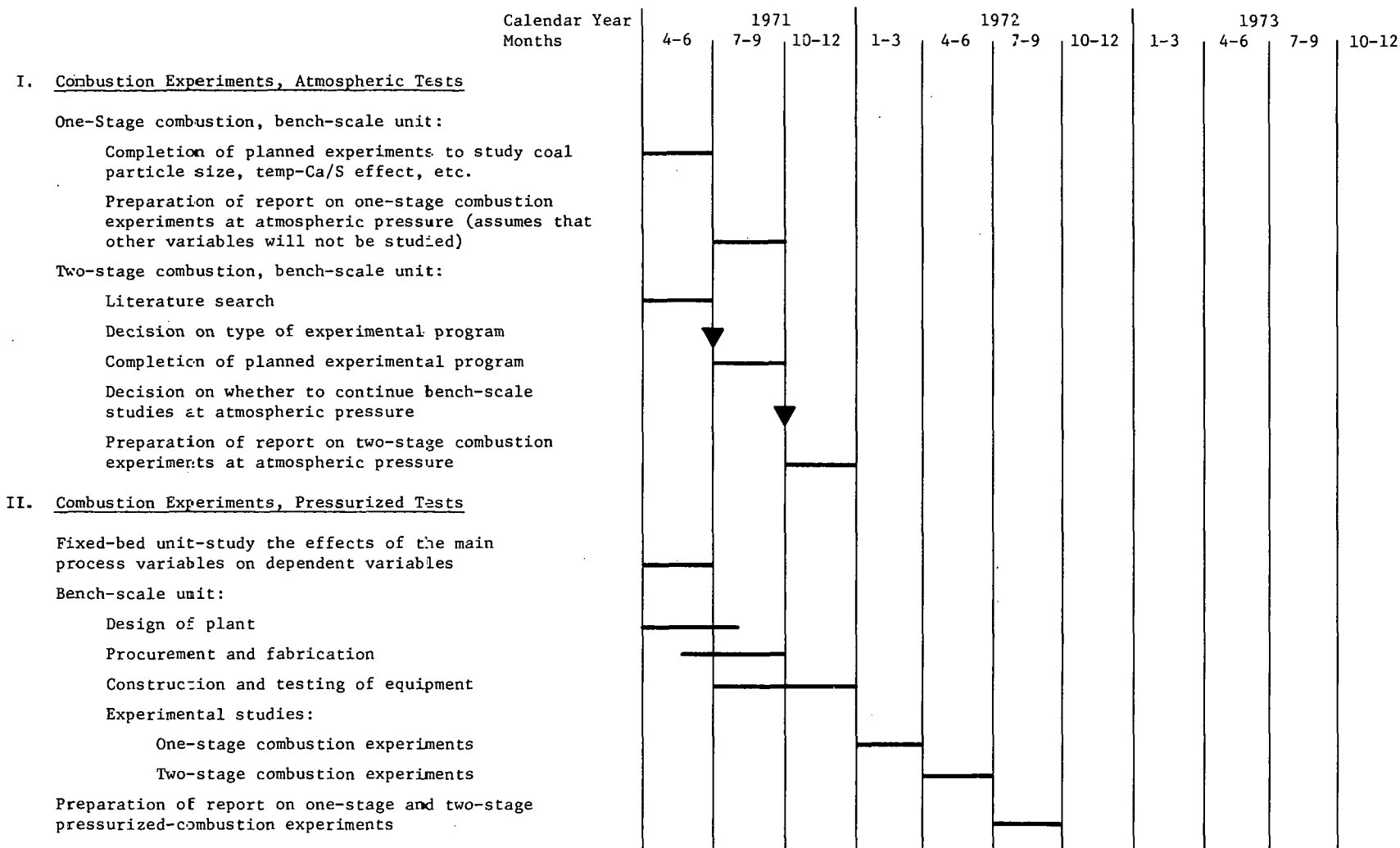
V. PROGRAM SCHEDULE AND MILESTONE CHART

The schedule of the development program is contingent upon the level of funding available. The attached milestone chart assumes that the current manpower level (June 15, 1970 to June 15, 1971) will be maintained constant and that funding will be provided for the construction of a new pressurized combustor-regenerator.

Emphasis in the future program will be given to the design, construction, and operation of the bench-scale pressurized unit for combustion and regeneration studies. Laboratory-scale work on pressurized combustion and regeneration will be continued, as well as work on the elucidation of mechanisms and related basic studies. Planned experiments on atmospheric-pressure combustions will be completed on a schedule that will not interfere with the work on pressurized combustion.

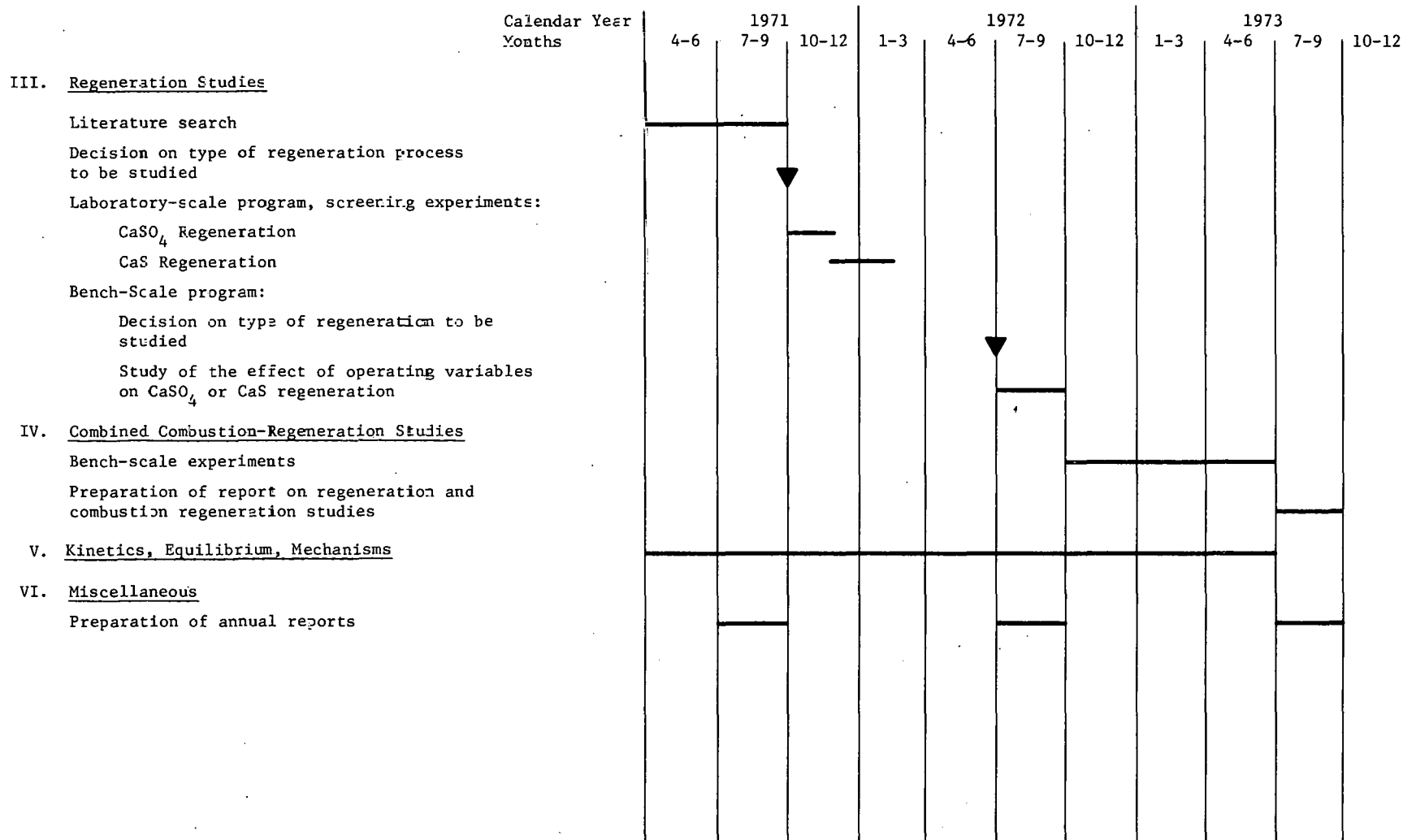
MILESTONE CHART

(Assumes Same Manpower Level as in Fiscal Year 1971)



MILESTONE CHART

(Assumes Same Manpower Level as in Fiscal Year 1971)



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