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SULPHUR NEUTRALIZATION BY LIGNITE ASH:  
PILOT-SCALE COMBUSTION EXPERIMENTS

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by

T. D. Brown\*, G. K. Lee\*\* and H. A. Bamborough\*\*\*

ABSTRACT

A pilot-scale research boiler (750 kg steam/h) was used to study the degree of sulphur neutralization during combustion experiments with three lignites.

A series of four closely controlled experiments showed that sulphur balances close to 100% could be achieved in the pilot-scale system burning Gascoyne lignite; the sulphur retained in solid phase residues varied between 21% and 24% of the input sulphur.

With Utility lignite, external recirculation of flue gas was moderately effective in reducing nitric oxide emissions, but led to increased carry-over of unburnt carbon. However, sulphur dioxide neutralization by coal-ash cations remained essentially unchanged as the recirculation ratio increased.

Enhancement of sulphur neutralization by dry lime addition to Poplar River lignite was effective only at addition rates above  $\frac{1}{2}$ % lime by weight. The effectiveness of the lime was found to increase as the excess-air level increased.

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## INTRODUCTION

A series of pilot-scale combustion experiments were conducted by the Canadian Combustion Research Laboratory (CCRL) to determine the degree of sulphur retention in ash when lignite was burned under conditions applicable to pulverized-fired utility boilers. The lignite samples contained less than one from North Dakota and two from Saskatchewan contained less than 0.7% sulphur on an as-received basis and moderate to high levels of alkaline ash constituents.

The test program was designed with a different objective for each of the three lignites. These objectives were:

1. To confirm the degree of sulphur neutralization by indigenous ash cations in Gascoyne lignite by means of a mass balance between input, retained and emitted sulphur.
2. To evaluate the effect of flue gas recirculation on  $SO_x$  emissions when Utility lignite was burned, and
3. To study the enhancement of sulphur retention in boiler ash deposits when Poplar River lignite was blended with lime upstream of the pulverizer.

This paper describes the pilot-scale test facility, the experimental procedures used and the results of the sulphur neutralization studies with the three lignites.

## EXPERIMENTAL BOILER

The experimental boiler, illustrated in Figure 1, has a full-load steaming rate of 750 kg/h (1600 lb/hr) at a pressure of  $10^6$  N/m<sup>2</sup> (150 psig). The firing system consists of two opposed burners inclined downward over a refractory-lined chamber. The furnace is of membrane-wall construction and will accept a maximum heat release rate of about  $0.9 \times 10^5$  W/m<sup>3</sup> ( $\approx 85,000$  Btu/ft<sup>3</sup>hr).

When the system is fired with pulverized coal, swirled secondary air is supplied via an annulus which is concentric with the pneumatic fuel supply. Both the primary and secondary air can be preheated up to 200°C.

Combustion gases leave the furnace at temperatures between 750°C and 900°C, pass through a transition section, then travel across the tubes of a high-temperature air heater. Finally, they pass through the tubes of a three-pass conventional air heater and enter the laboratory exhaust system via a breeching, at temperatures between 250°C and 400°C. For external flue-gas recirculation, a high-pressure blower connected to the breeching supplies controlled quantities of flue gas at 200°C to the secondary-air annuali of the burners. This provides variable blends of oxygen-lean flue gas and secondary combustion air for participation in the combustion process. There is also provision to recirculate the flue gases both above and below the flames.

The boiler is manually controlled except for some electrical interlocks to ensure a safe start-up and shutdown procedure.

The usual operating procedure was to bring the boiler to an equilibrium thermal condition for each experiment. When thermal equilibrium was established, the performance parameters of interest were measured continuously.

#### Experimental Measurements

The following measurements, taken during each combustion trial, provided data for a complete sulphur balance between the sulphur in the fuel and the residual sulphur in the combustion produces and enabled evaluation of the effect of selected experimental strategies on sulphur retention in ash.

- Proximate and ultimate analysis of one daily coal sample compiled from hourly grab samples of the feed to the pulverizer;
- Fuel feed rate of 180 kg/h, recorded at  $\frac{1}{2}$ -hourly intervals from a continuous electronic weighing system on the fuel storage hopper;
- Moisture and sulphur determinations of the pulverized coal feed to the burners at hourly or  $\frac{1}{2}$ -hourly intervals; these measurements were used only to indicate the variability in sulphur content of the coal throughout the experiment;
- Flue-gas analysis; CO<sub>2</sub>, CO and O<sub>2</sub> measured continuously by infra-red or paramagnetic monitors;

- Nitric oxide content of the flue gases, measured continuously by chemiluminescent monitor;
- Sulphur dioxide concentration measurements in the flue gases, made intermittently using the Environment Canada technique 1-AP-74-1(1);
- Sulphur trioxide concentration measurements in the flue gas, made intermittently using Environment Canada technique 1-AP-74-1(1);
- Fly-ash loading, measured intermittently using Environment Canada (1) isokinetic sampling technique at least twice during each experiment; these samples were analyzed for moisture and sulphur;
- Electrostatic precipitator efficiency, measured by passing part of the flue gases through a small single-field electrostatic precipitator;
- Moisture and sulphur determinations, made on composite samples of the total boiler deposit recovered from each of the seven designated areas within the boiler; these samples were recovered by brushing and vacuuming the entire unit 12 hours after the end of each experiment;

#### LIGNITE ANALYSES

The analyses of the three lignite samples are given in Table 1. The Gascoyne and the Utility lignites, from southwestern North Dakota and southeastern Saskatchewan respectively, are both mined commercially. The Poplar River lignite deposit, located in southwestern Saskatchewan, is currently being developed.

#### SULPHUR BALANCE DETERMINATIONS

Four combustion experiments were conducted to determine the extent to which a sulphur balance could be achieved when Gascoyne lignite was burned under controlled conditions in the CCRL pilot-scale research boiler. These experiments were designed to determine accurately the fuel sulphur input; the sulphur emissions to atmosphere as gaseous oxides and sulphated ash; and the sulphur retained in the residual boiler ash.

### Sulphur Balance Data

To compensate for the fact that the intermittent sampling systems could not be operated simultaneously and the boiler deposits could only be collected as a single composite sample at the end of each test, it was essential to operate with all combustion conditions constant. Mass balances, whether for sulphur or any other coal constituent, can only be drawn up with confidence if the input conditions of feed rate, fuel sulphur content and excess-air level are held within close steady-state tolerances during an experiment.

Sulphur Input: The hourly mass input of coal to the pulverizer was used in conjunction with the sulphur analysis of a composite sample of the coal feed to provide the mass input rate of sulphur for each combustion experiment. The sulphur input rates for each test are shown in Table 2.

Sulphur Dioxide: Gas-phase sulphur dioxide measurements were made repetitively throughout each experimental run.

In determining the total gas-phase sulphur emission for Test No. 1 the total combustion product volume was calculated from the excess-oxygen in the flue gas, the ultimate analysis of the coal feed and the coal feed rate, and used in conjunction with the measured sulphur dioxide concentration to determine the sulphur dioxide output in kg/h. For Tests No. 2, 3 and 4 a measured volumetric gas flow rate was used.

Sulphur Trioxide: During Tests No. 2, 3 and 4, measured sulphur trioxide concentrations were in the range 21 ppm - 24 ppm. These measurements were used in conjunction with volumetric flow rates to calculate the sulphur trioxide output.

Sulphur in Particulate Matter: Mass concentrations of gas-borne particulate matter at the precipitator inlet were measured during each test and the solid material was analyzed for moisture and sulphur content. Isokinetic samples were taken on a four-point grid during Test No. 1 using a CCRL developed system. During Test No. 2 an eight-point vertical cumulative sample was taken and during Tests No. 3 and 4 both an eight-point vertical cumulative sample and a sixteen-point (8 vertical, 8 horizontal) cumulative sample were using an emission sampling train approved by Environment Canada.



The fly ash samples collected were analyzed for moisture and sulphur content. These analyses were used, in conjunction with the measured volumetric flow rates for each test, to calculate the sulphur output in the gas-borne particulate material.

Sulphur Retained in Boiler Deposits: The mass and sulphur content of the boiler deposits were used to establish the total sulphur retained within the boiler over the duration of each combustion test.

Sulphur Accountability: Sulphur balances, compiled for all four tests, showed that over 80% of the input sulphur could be accounted for. In all cases the results, presented in Table 2, show clearly that when rigorous care is taken during all sampling procedures, a sulphur balance to within 10% of the input condition can be achieved. The corollary of this conclusion is that, given the same stringent control of both the boiler system and the sampling techniques, measurement of the gas-phase sulphur dioxide and trioxide concentrations can be used to estimate the extent of sulphur neutralization by cations in the coal ash.

Previous experimental work by Gronhovd et al(2) on a series of utility boilers burning North Dakota lignites led to development of an expression describing the gas-phase sulphur emissions in terms of the ash analysis:

$$\text{Gas-phase Sulphur Emitted} = 110.0 - 12.7 \left[ \frac{\text{CaO}}{\text{Al}_2\text{O}_3} \right] - 48.1 \left[ \frac{\text{Na}_2\text{O}}{\text{SiO}_2} \right]$$

The numerical expression was based solely on gas-phase sulphur dioxide measurements. Application of this equation to the ash analysis of the coal used in four independent sulphur balance experiments leads to the following results for sulphur retained in boiler deposits and fly ash.

<u>Calculated from Gronhovd</u>	<u>Sulphur in Fly-ash and Retained in Boiler Deposits</u>
23.2	24.5
20.5	23.2
20.5	20.6
20.5	21.0

### Sulphur Emissions at the Precipitator Outlet

Sulphur emissions to atmosphere after electrostatic gas cleaning include the gas-phase sulphur oxides and the sulphur in the uncollected particulate material. During Tests No. 1 and 4 a small, single-field electrostatic precipitator was used to clean a portion of the gas stream and to measure a precipitator collection efficiency.

The fine particulate material collected at the precipitator outlet was analyzed for moisture and sulphur content and the data were used to calculate the total sulphur emissions from the system at the precipitator exit. The sulphur in the emitted particulate material constituted less than 0.03% of the total input sulphur and less than 0.05% of the total sulphur emission. Therefore, in a practical system equipped with high-efficiency (+98%) dust collection, the sulphur in the emitted fly-ash could be omitted with no measureable effect on the accuracy of a sulphur balance.

### EXPERIMENTS WITH EXTERNAL FLUE GAS RECIRCULATION

External flue gas recirculation experiments with Utility lignite were conducted at both full-load and part-load with excess-air level and recirculation ratio being superimposed variables.

The definition of recirculation ratio adopted in these experiments was that of Hedley(3):

$$\text{Recirculation Ratio, } R = \frac{M_r}{M_r + M_a + M_f},$$

where  $M_a$ ,  $M_f$  and  $M_r$  are the mass flows of air, fuel and recirculation flue gases respectively.

The effect of NO and combustible emissions from the research boiler due to introduction of recirculated flue gas into the secondary air supply to each burner is shown in Figures 2 and 3.

Figure 2 shows that reductions in excess-oxygen level from 5% to 1% resulted in a reduction in the nitric oxide emission of about 50%. Figure 3 shows that this did not result in a major increase in the unburnt carbon content of the fly-ash.

The introduction of externally recirculated flue-gas ( $R = 0.3$ ) produced reductions in nitric oxide emissions between 30% and 50% depending on the excess-air level (Figure 2).

Figure 4 shows that the thermal penalty associated with the combustible content of the fly ash was only slightly affected by low excess-air combustion, but was markedly affected by recirculation ratios above 0.1.

An important emission control process which occurs naturally in coals with alkali and alkaline-earth ash constituents is the neutralization of  $SO_2$  by metal ions in the ash. This can significantly reduce the  $SO_2$  concentrations in the flue-gas. Table 3 shows that neither excess-oxygen level nor external flue-gas recirculation had a major effect on the extent of sulphur neutralization.

It appears from the experimental data that low excess-air combustion is a more practical  $NO$  control technique than flue-gas recirculation. It offers prospects of control without the thermal penalty associated with recirculation. The magnitude of the reductions achieved by external flue gas recirculation at excess-oxygen levels of 3% and 5% suggests that a significant proportion (>50%) of the nitric oxide produced during combustion of this fuel came from atmospheric nitrogen.

The thermal penalty associated with combustible carry-over in the fly-ash is dependent on both the excess-air level and the recirculation ratio as well as burner geometry. If external flue-gas recirculation is to be used as a nitric oxide control measure it may be necessary to increase excess-air levels to maintain combustion efficiency. Under such conditions, a boiler efficiency penalty will be incurred and an optimization of the conflicting parameters should be undertaken before flue gas recirculation is utilized as a  $NO_x$  strategy.

#### ENHANCED SULPHUR NEUTRALIZATION BY LIME ADDITION

For the lime addition experiments, one-ton batches of Poplar River lignite were blended with pebble lime (<1/8") in a rotary riffle to ensure uniform distribution of the lime throughout the fuel prior to pulverizing.

### Sulphur Dioxide Emissions

SO<sub>2</sub> neutralization measured in each combustion experiment is presented in Figure 5; no sulphur trioxide was detected during any of the combustion experiments. SO<sub>2</sub> was increased by addition of 1 wt% lime to the fuel whereas a ½ wt% had no significant effect.

The results at 1 wt% lime addition showed an increase in SO<sub>2</sub> neutralization with increasing partial pressure of oxygen, i.e. excess-air level. With 1 wt% lime addition to the fuel, the degree of sulphur neutralization due to indigenous cations in the raw lignite was about 32% for nominal excess air levels corresponding to 1%, 3% and 5% O<sub>2</sub> in flue gas.

### Lime Utilization

By assuming an overall reaction of the form



the lime utilization with 1 wt% lime in the coal was calculated to be 14.7%, 15.9% and 24.6% at excess oxygen levels of 1%, 3% and 5% respectively. This suggests that complete elimination of SO<sub>2</sub> will require a minimum lime addition rate of 2%, which corresponds to an atomic ratio Ca:S = 3:1. The sub-stoichiometric lime reactivity observed in these tests may have been affected by calcination temperature during either lime production or exposure in the lignite flame since a dead burnt lime with its consequent low porosity has a low reactivity with respect to SO<sub>2</sub>. In addition, sulphur reaction rates with calcium are strongly dependent on the contact time available in the 1400°F - 1900°F temperature zone of the furnace.

### Fly-ash Characteristics

The consistently high fly-ash loadings at the highest excess-air levels are probably due to the increased gas velocity which in turn minimized gravity settling of dust throughout the boiler. The lime additive experiments showed that the thermal penalty due to unburnt carbon in the fly-ash remained unchanged.

The performance of the laboratory electrostatic precipitator did not change as the neutralization of the SO<sub>2</sub> was increased by lime addition.

## CONCLUSIONS

Under carefully controlled conditions it has been shown possible to account for more than 90% of the input sulphur when Gascoyne lignite was burned in a pilot-scale boiler. Under field conditions, rigorous sampling techniques will therefore allow determination of the extent of sulphur neutralization from measurements of the sulphur input and the gas-phase sulphur oxides. The experiments also confirm the applicability (for lignites) of predictions based on ash analysis.

Sulphur neutralization with Utility lignite was unaffected by the use of external flue-gas recirculation as a nitric oxide control measure; the control technique produced unacceptable thermal penalties due to carbon carry-over when used in conjunction with low excess-air combustion.

Sulphur neutralization by lime addition to Poplar River lignite prior to the pulverizer was enhanced only at addition rates of 1%. Lime utilization increased with increasing excess air up to a maximum of 25% at excess-oxygen levels of 5%.

## REFERENCES

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2. H. Gronhovd, P. H. Tufte and S. J. Selle, "Some Studies on Stack Emissions from Lignite-fired Power Plants". 1973 Lignite Symposium, Bismarck, North Dakota, U.S.A.
3. A. B. Hedley and E. W. Jackson, "Recirculation and Its Effect on Combustion Systems". J Inst Fuel 1965 Volume 38 pp 39.

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TABLE 1

Analyses of the Experimental Lignites  
(The Coal Feed to the Pulverizer)

Lignite		Gascoyne	Utility	Poplar River
Analysis				
Moisture	%	38.72	17.06	12.91
Ash	%	7.65	11.11	17.30
Volatile Matter	%	27.11	32.51	33.23
Fixed Carbon	%	27.52	39.32	36.56
Carbon	%	38.08	50.60	49.11
Hydrogen	%	2.59	3.31	3.21
Sulphur	%	0.74	0.48	0.60
Nitrogen	%	0.64	0.87	0.66
Ash	%	7.65	11.11	17.30
Oxygen	%	11.58	16.57	16.21
Gross Calorific Value	cal/g	3530	4570	4410
Hardgrove Grindability			56	65
Ash				
SiO <sub>2</sub>	%	33.23	26.57	44.14
Al <sub>2</sub> O <sub>3</sub>	%	10.03	15.77	22.10
Fe <sub>2</sub> O <sub>3</sub>	%	5.10	6.43	5.63
TiO <sub>2</sub>	%	0.51	0.58	1.02
P <sub>2</sub> O <sub>5</sub>	%	0.25	0.74	0.27
CaO	%	20.09	22.54	12.67
MgO	%	7.56	4.13	4.18
SO <sub>3</sub>	%	18.77	14.13	7.97
Na <sub>2</sub> O	%	3.55	6.78	0.70
K <sub>2</sub> O	%	0.60	0.37	1.60

TABLE 2

Sulphur Balances for Gascoyne Lignite

Test No.		1	2	3	4
Sulphur Data					
Sulphur Input	kg/h	0.912	0.999	0.956	0.956
Sulphur Outputs	kg/h				
as SO <sub>2</sub>		0.530	0.740	0.780	0.776
as SO <sub>3</sub>		-	0.018	0.016	0.018
Particulates		0.073	0.089	0.081	0.085
Sulphur Retained in Boiler	kg/h	0.150	0.143	0.116	0.116
Total Accountable Sulphur	kg/h	0.753	0.990	0.993	0.995
Accountable Sulphur					
as % of Input		82.6	99.1	103.9	104.2

TABLE 3

Effect of Recirculation Ratio on Sulphur Neutralization  
During Combustion of Utility Lignite

Nominal Excess Oxygen Level %	Recirculation Ratio	% SO <sub>2</sub> Neutralization*
5	0.00	54
	0.20	47
	0.23	49
	0.26	54
3	0.00	48
	0.23	51
	0.27	50
	0.28	50
1	0.00	43
	0.26	43
	0.27	58
	0.30	46

\*% SO<sub>2</sub> Neutralization =  $\frac{\text{SO}_2 \text{ theoretical} - \text{SO}_2 \text{ measured}}{\text{SO}_2 \text{ theoretical}} \times 100$



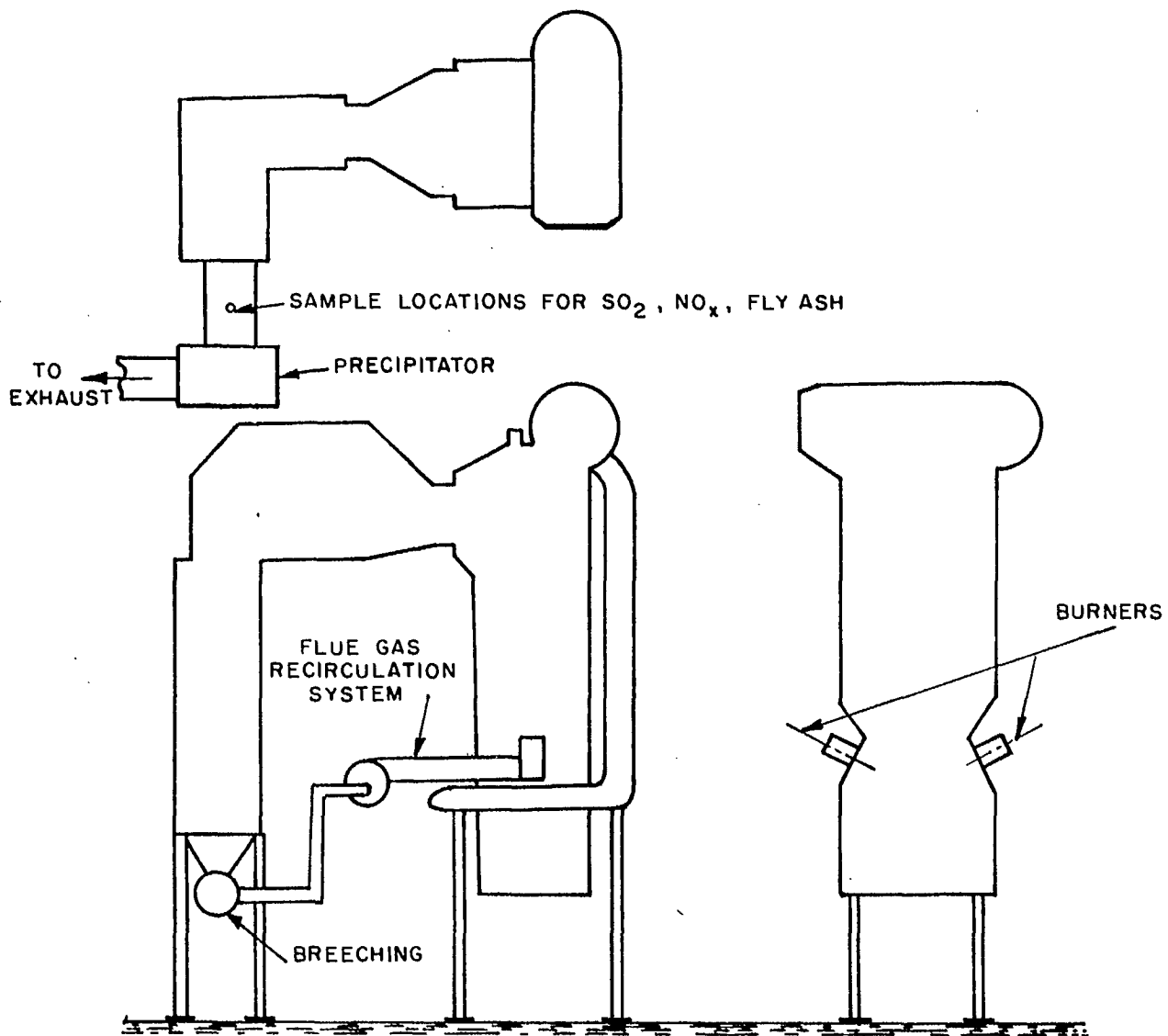


FIGURE 1. SCHEMATIC OF THE PILOT-SCALE RESEARCH BOILER.

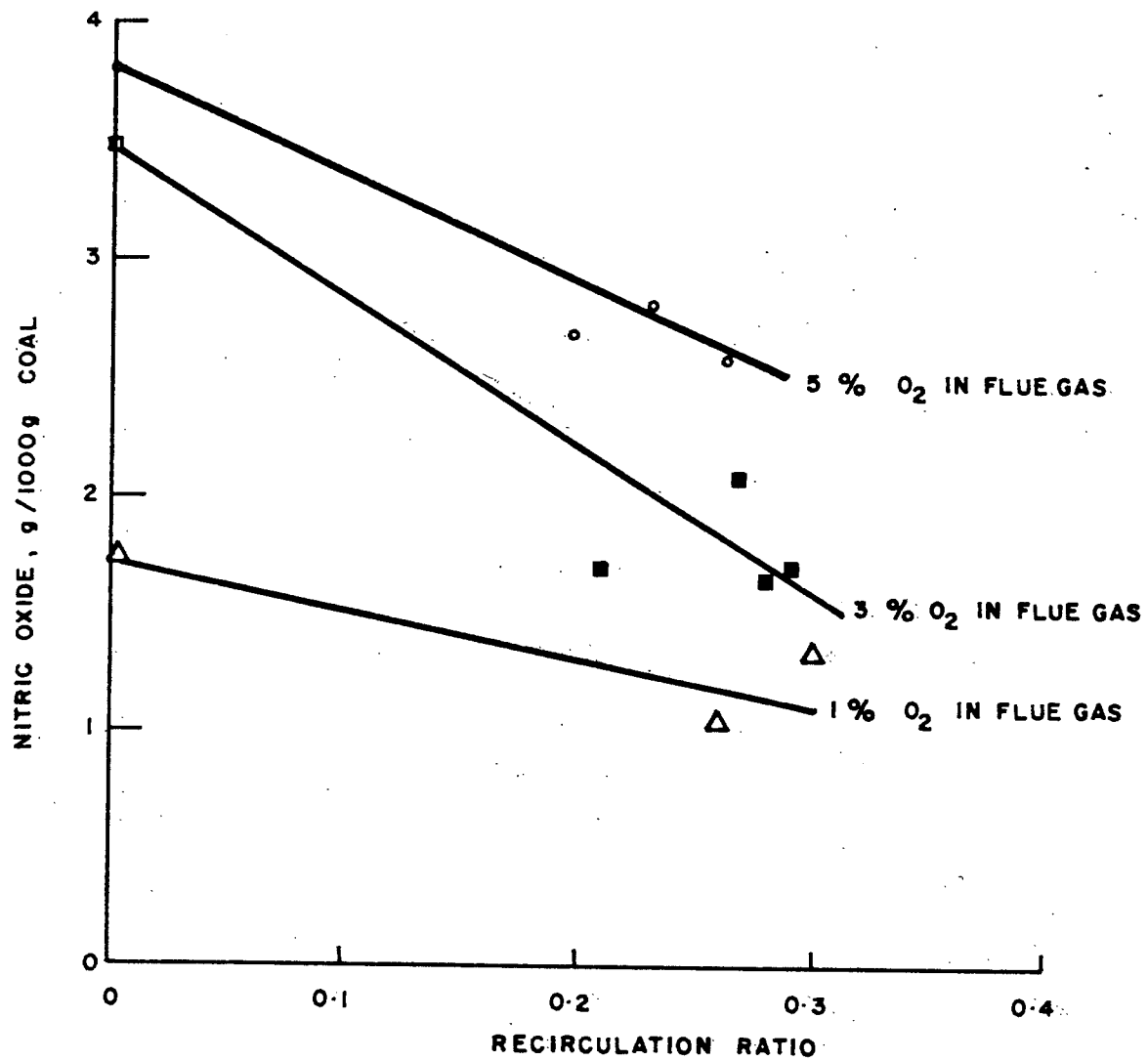


FIGURE 2. EFFECT OF RECIRCULATION ON NITRIC OXIDE EMISSIONS FROM UTILITY LIGNITE.

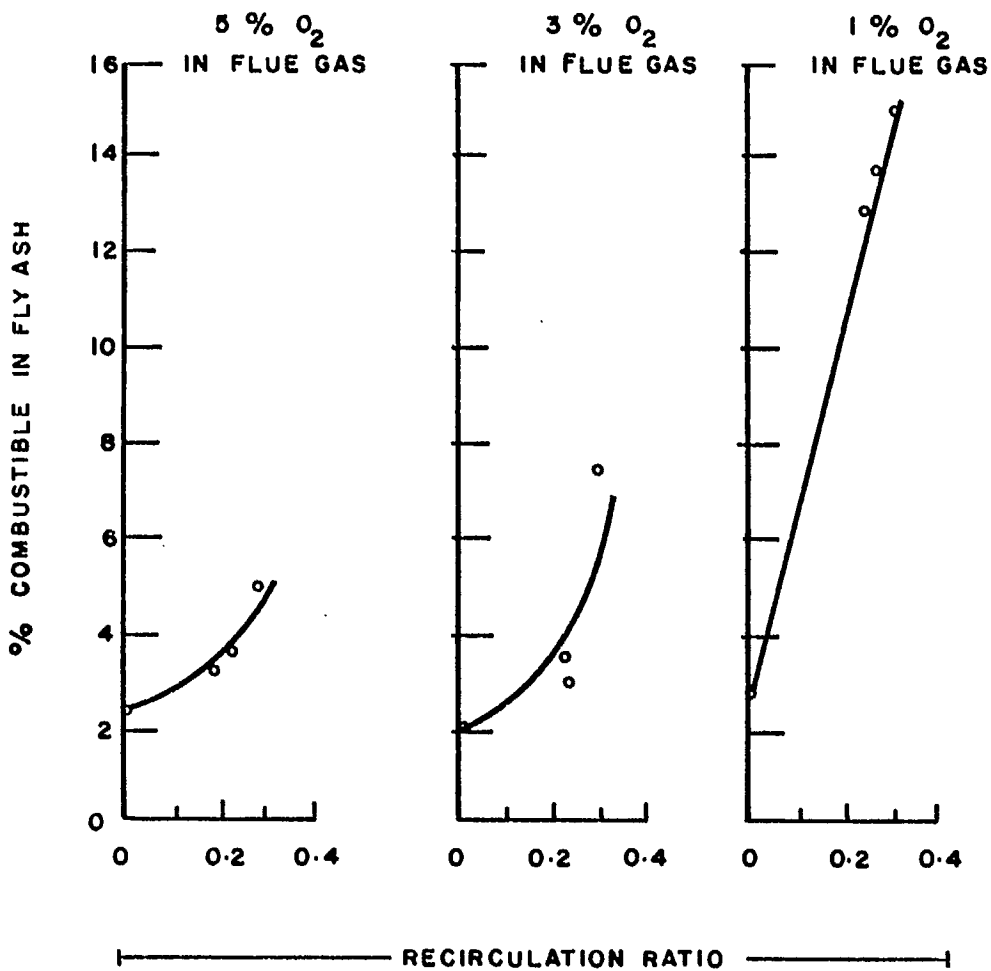


FIGURE 3. EFFECT OF RECIRCULATION RATIO AND EXCESS-AIR LEVEL ON THE FLY ASH FROM UTILITY LIGNITE COMBUSTION.

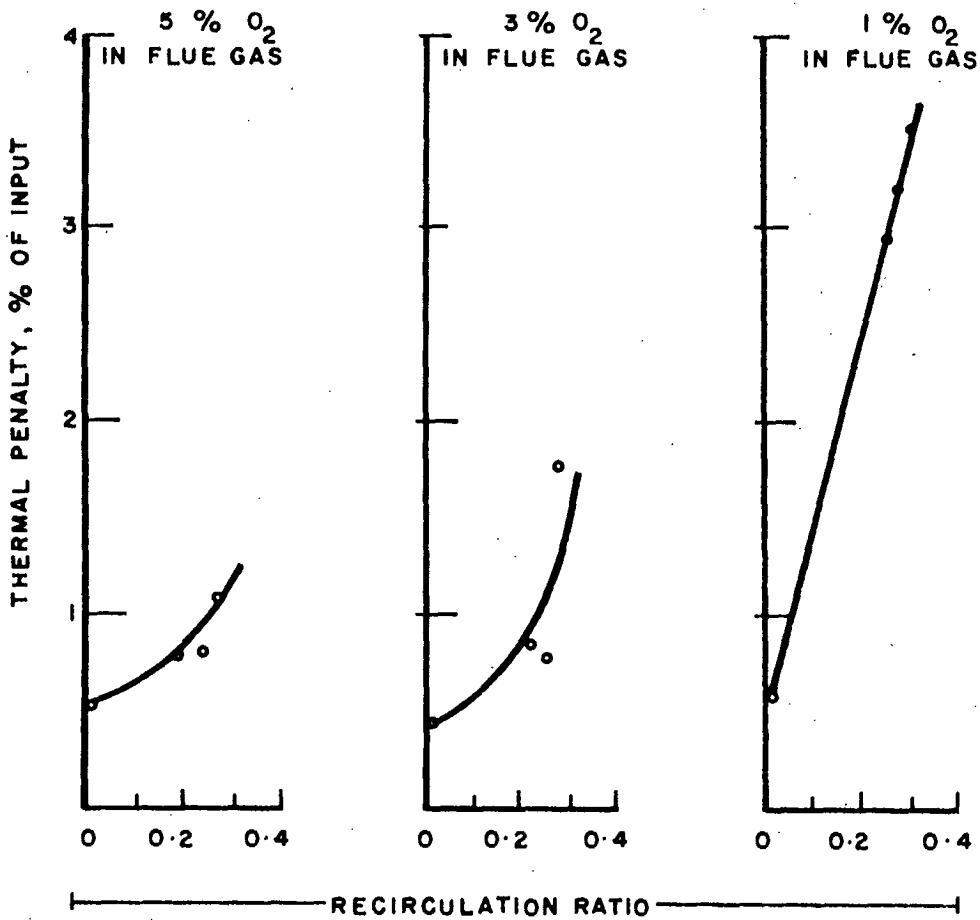


FIGURE 4. EFFECT OF RECIRCULATION RATIO ON THE THERMAL PENALTY DUE TO UNBURNT CARBON IN THE FLY ASH FROM UTILITY LIGNITE COMBUSTION.

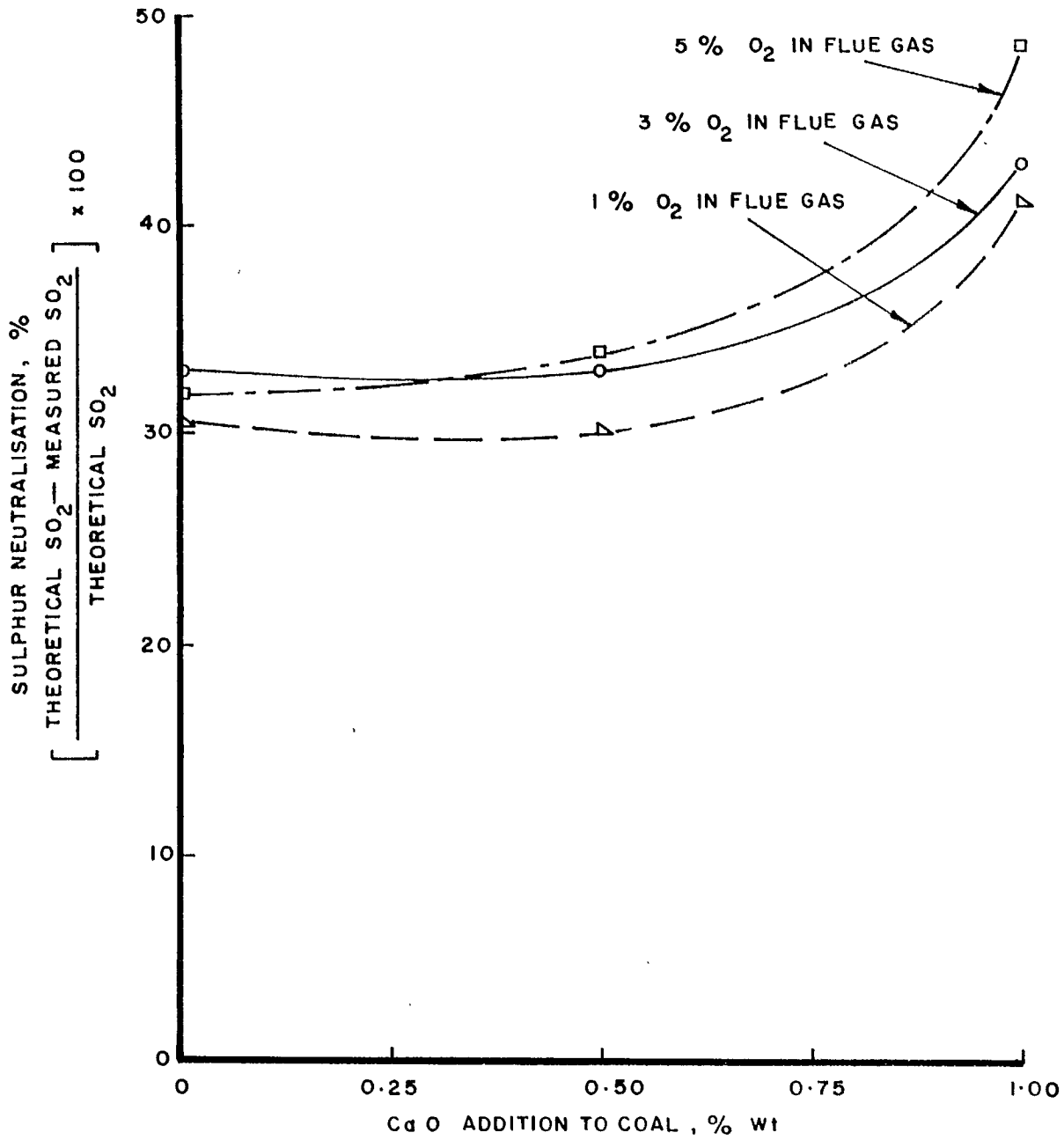


FIGURE 5. EFFECT OF LIME ADDITION ON SULPHUR DIOXIDE NEUTRALIZATION DURING COMBUSTION OF POPLAR RIVER LIGNITE.