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EFFECT OF CALCIUM-BASED ADDITIVES ON DEPOSITS
AND EMISSIONS FROM PULVERIZED-COAL FLAMES

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ABSTRACT

A bituminous coal blend containing 1.7% sulphur and 11% ash was burned in a pilot-scale research boiler to evaluate the influence of limestone and dolomite additions, with and without calcium chloride treatment, on boiler performance, ash deposition and acid gas emissions.

Additive dosage rates of $(Ca + Mg) / S = 3$ produced dusty, but moderately heavy fireside deposits and a 32% reduction in sulphur oxide emissions. Calcium chloride treatment with the same additive dosage rate resulted in total blockage of the convection passes and a further 28% reduction in sulphur oxide emissions. This incremental sulphur oxide reduction was, however, offset by an equivalent increase in chloride emissions and a significant increase in the chloride content of the furnace deposits.

INTRODUCTION

Emissions of sulphur oxides from pulverized coal-fired boilers can be reduced significantly by injecting alkaline earth minerals into the flame zone (1). However, in some installations, this control measure can result in accelerated fouling and slagging of fireside surfaces and overloading of the ash collection and removal system, because sorbent utilization is typically less than 30%. Enhancement of sulphur capture by small additions of chloride to the sorbent has been successful in fluid-bed combustion systems (2), but

this technique has not been studied extensively in pulverized coal systems where total chloride in the coal feed is limited typically to less than 0.3% to minimize metal corrosion.

This paper evaluates the influence of limestone and dolomite additions, with and without calcium chloride treatment, on acid gas emissions during a series of combustion trials in a pilot-scale, pulverized-coal-fired boiler. The effect of these additives on steaming rate, combustion efficiency and ash deposition characteristics is also described.

COAL AND SORBENT MIXES

The analyses of the coal and the sulphur sorbents evaluated are given in Tables 1 and 2. Prior to pulverizing, the test coal was premixed with either limestone or dolomite with the liquid calcium chloride solution being added to the sorbent-treated coal at the pulverizer inlet as required. The test matrix for the trials is given in Table 3.

PILOT-SCALE RESEARCH BOILER

The research boiler, shown schematically in Figure 1, is equipped with two opposed, pulverized coal burners which are direct fired from a ring-roller mill containing a motor-driven classifier. Combustion air at 260°C and 7 kPa is supplied to both the pulverizer and the burners by a forced draft fan (3).

Figure 1 also shows the locations of the sampling stations where the following parameters were monitored:

- a) coal feed quality, pulverizer inlet;
- b) moisture and sieve analysis of pulverized coal, pulverizer outlet;
- c) slagging propensity on refractory, Station 1;
- d) furnace wall deposition, Station 2;
- e) screen tube fouling tendency, Station 3;
- f) superheater fouling tendency, Station 4;
- g) flue gas analyses of CO₂, O₂, NO_x and SO₂, Station 5;
- h) in situ fly ash resistivity at 150°C, Station 6;
- i) fly ash loading, composition, combustible content, and size distribution, Station 7;
- j) electrostatic collection efficiency, Station 8.

TABLE 1

COAL AND COAL ASH PROPERTIES

COAL ANALYSIS			
PROXIMATE, % DRY		ULTIMATE, % DRY	
ASH	11.1	C	73.3
VOLATILE MATTER	33.5	H	4.4
FIXED CARBON	55.4	S	1.7
		N	0.9
		O	5.6
		Cl	0.1
CALORIFIC VALUE, DRY		29.7M J/KG	
MOISTURE, AS REC'D		4.7%	
HARDGROVE INDEX		52	
FREE SWELLING INDEX		1 1/2	
SIZE CONSIST: 25MM		91%	
	6MM	53%	
COAL ASH COMPOSITION, WT%			
SiO ₂	48.7	MgO	1.0
Al ₂ O ₃	19.3	SO ₃	4.2
Fe ₂ O ₃	17.1	Na ₂ O	0.7
Ca O	5.6	K ₂ O	1.0
TiO ₂	0.9		
ASTM COAL ASH FUSIBILITY, °C			
ATMOSPHERE TEMPERATURE	OXIDIZING	REDUCING	
INITIAL	1271	1118	
SPHERICAL	1321	1227	
HEMISPHERICAL	1352	1327	
FLUID	1393	1343	

TABLE 2

ALKALINE SORBENT ANALYSIS

ANALYSIS	LIMESTONE	DOLOMITE	CALCIUM CHLORIDE
COMPOSITION, %WT			
SiO ₂	2.4	7.6	
CaO	39.5	48.5	
MgO	12.4	1.7	
LOF	45.6	40.5	
Ca			27.7
Cl	0.01	0.02	49.3
H ₂ O			23.0
SIZE CONSIST:			
250 μ m	97	95	SOLUTION
74 μ m	69	32	

TABLE 3

TEST MATRIX

TEST No.	DOLOMITE	LIMESTONE	CALCIUM CHLORIDE*	Ca+Mg:S MOL RATIO
1	-	-	-	0.2
2	x			2.1
3	x			4.2
4	x		x	2.2
5	x		x	4.5
6		x		1.5
7		x		3.0
8		x	x	1.6
9		x	x	3.2

*CaCl₂ _ 5% ADDITIONAL Ca-

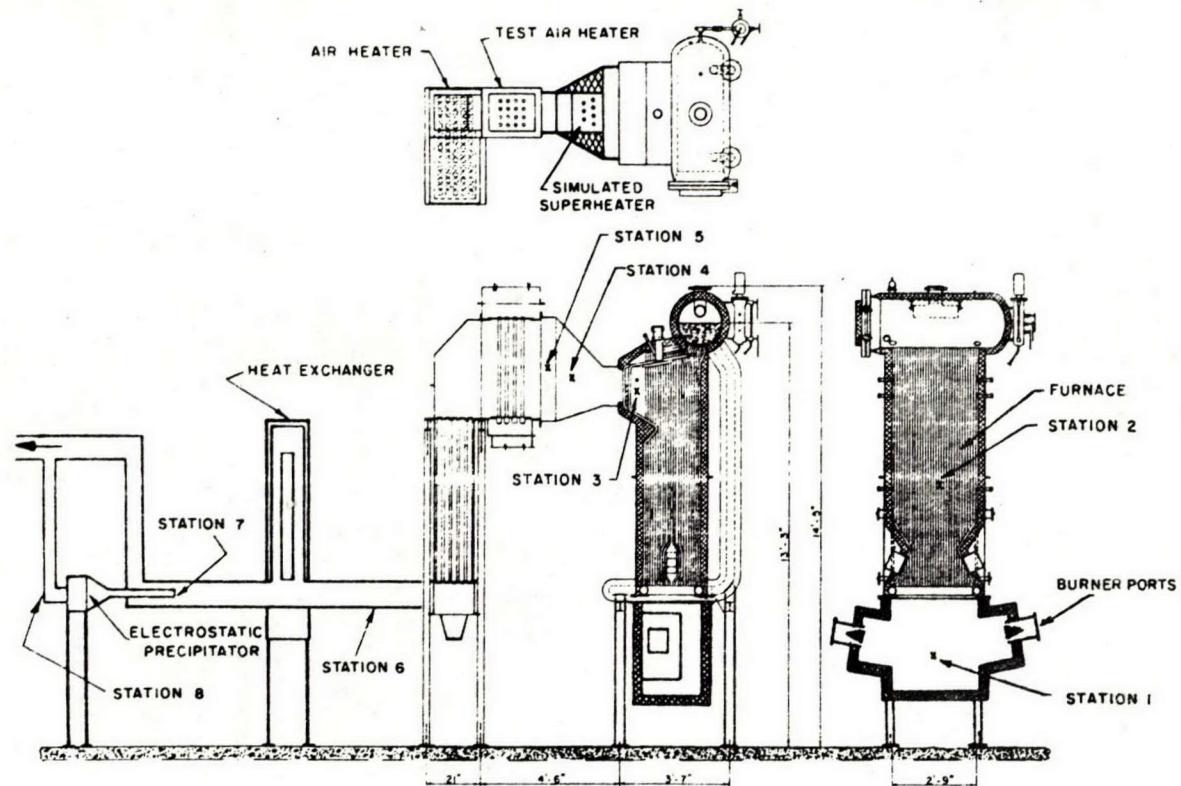


FIGURE 1. Pilot-scale research boiler.

EXPERIMENTAL

Boiler Operating Conditions

The boiler operating conditions for each trial in the experimental matrix were controlled nominally at the values given in Table 4. Figure 2 illustrates the steady decline in steaming rate and the corresponding increase in furnace exit temperature that occurred with increases in ash deposition on the furnace walls due to increases in the $(Ca + Mg) / S$ mol ratio. Soot blowing to control ash build-up was omitted during these trials.

Acid Gas Emissions

Figure 3 shows the effect of additive treatment on the acid gas emissions. Increases in $(Ca + Mg) / S$ ratios reduced sulphur oxide emissions progressively, but had no effect on nitrogen oxide emissions. Liquid calcium chloride additions to the limestone or dolomite corresponding to a 5% increase in calcium treatment produced a further reduction in sulphur oxide emissions at the same $(Ca + Mg) / S$ ratios, but again had no effect on nitrogen oxide emissions. Unfortunately, the additional reductions in sulphur oxides due to chloride treatment were more than offset by increased chloride emissions.

Figure 4 is a replot of Figure 3 showing the percentage neutralization of sulphur oxides and chloride due to additive treatment. At a $(Ca + Mg) / S$ ratio of 3 about 32% of the input sulphur was fixed in the ash by limestone or dolomite additions; this was increased to 60% by a calcium chloride addition, corresponding to a 5% increase in calcium treatment. However, the additional sulphur neutralization due to the addition of calcium chloride to either limestone or dolomite, was nullified by the low retention, less than 20% of the input chloride, by ash constituents.

Fly Ash Characteristics

The fly ash loadings, Figure 5, increased linearly with $(Ca + Mg) / S$ ratios due to limestone or dolomite alone. With calcium chloride additions to the limestone or dolomite the fly ash became so sticky at $(Ca + Mg) / S$ ratios over 2 that the fly ash loadings to the precipitator rapidly decreased due to an accelerated build-up of ash on convective heat transfer surfaces.

TABLE 4

BOILER OPERATING CONDITIONS

BOILER OPERATING CONDITIONS	
COAL RATE, KG/H	74
COAL FINENESS, % 74 μ m	78
HEAT INPUT, MJ/H	2100
CO ₂ , %	14.8
O ₂ , %	3.7
CO, PPM	50
COMBUSTIBLE IN FLY ASH, %	3
COMBUSTION EFFICIENCY, %	99.6 - 99.7

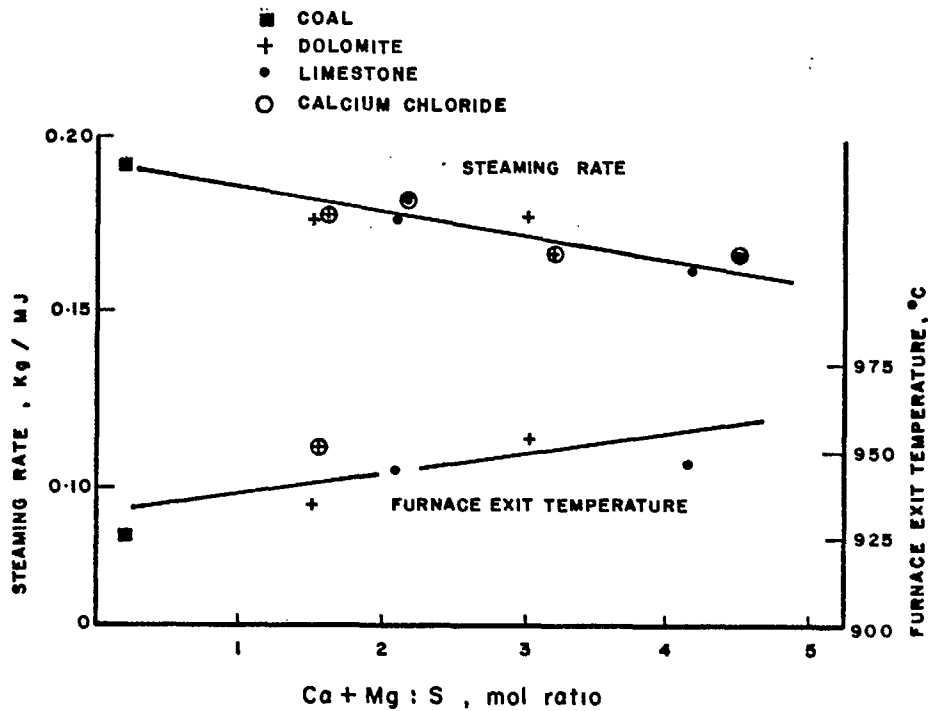


FIGURE 2. Effect of sorbent additions on steaming rate and furnace exit temperature.

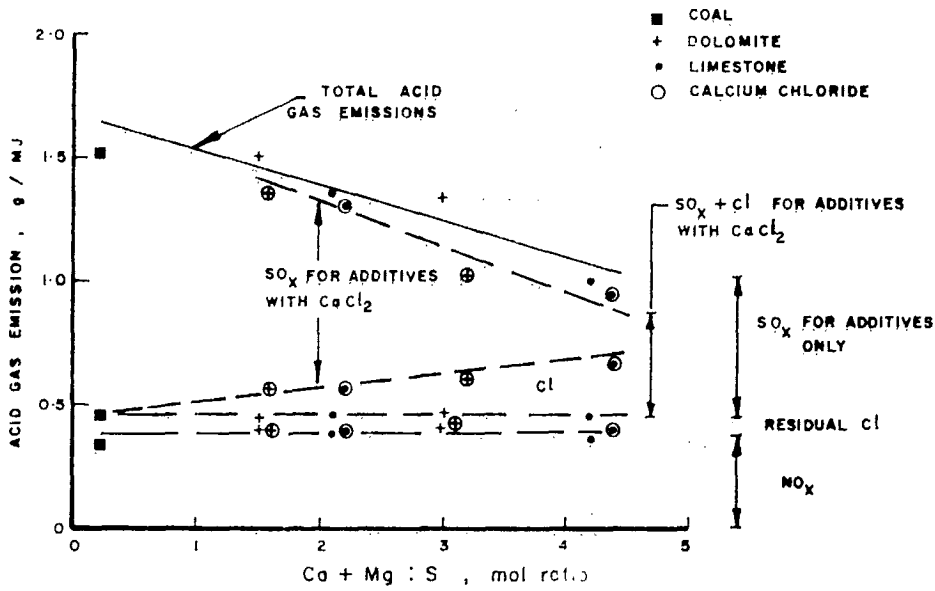


FIGURE 3. Effect of sorbent additions on acid gas emissions.

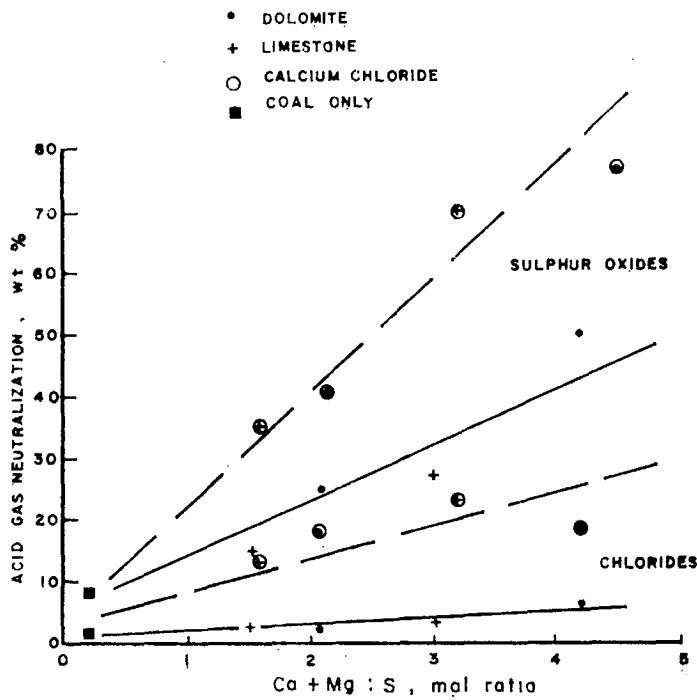


FIGURE 4. Sulphur oxide and chloride neutralization by sorbents.

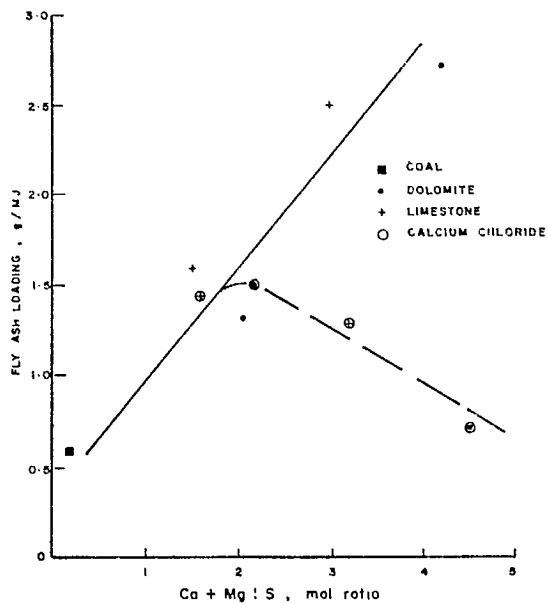


FIGURE 5. Fly ash loadings at various Ca + Mg:S ratios.

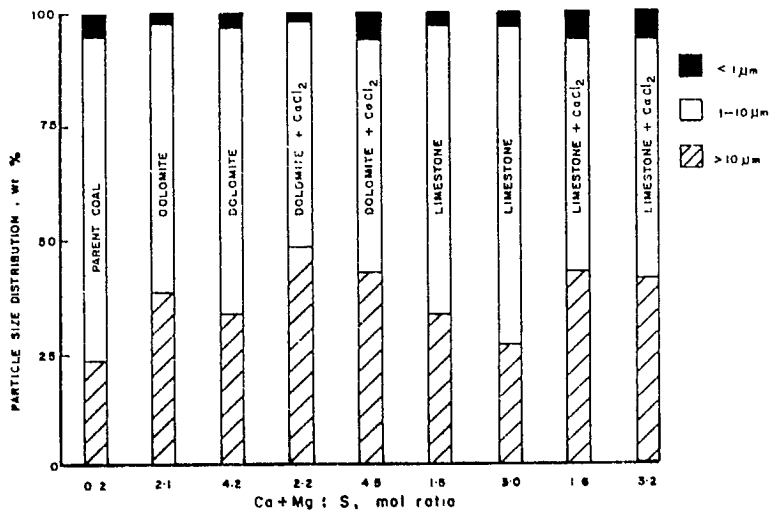


FIGURE 6. Particle sizes of fly ash at precipitator inlet.

Figure 6 shows that the addition of calcium chloride increased the mass fraction of ash particles under 1 μm . This indicates that the chlorides caused fracturing of the limestone and dolomite particles thereby creating extended surfaces for sulphur neutralization. The mass fraction of +10 μm ash particles fell from 25% to 50% of the total ash and were not significantly affected by chloride treatment.

During all trials, in situ fly ash resistivities ranged from 10.6 to 11.6 log ohm-cm at 150°C and carbon in fly ash was consistently less than 3%, indicating that the performance of electrostatic precipitators would unlikely deteriorate with additive treatment. This observation was confirmed by measurements taken at the end of each trial which showed that the collection efficiency of the experimental precipitator had exceeded 98%.

Figure 7 shows that the basic oxide composition of the fly ash was reduced slightly by calcium chloride additions to the limestone and dolomite.

Ash Slagging and Fouling Tendency

The potential slagging temperatures and the basic oxide constituents of the furnace bottom and superheater ash deposits, shown in Figures 8 and 9, respectively, indicate a severe to high slagging propensity for the furnace bottom ash. This prediction was confirmed by the presence of molten slag deposits in the furnace bottom, Figure 10, at the end of each trial; calcium chloride additions had no observable effect on slagging.

Fouling of the superheater tubes, shown in Figure 11 and 12, increased progressively as the $(\text{Ca} + \text{Mg}) / \text{S}$ ratio increased. Additions of calcium chloride transformed these normally loose, powdery deposits to a sticky ash with enriched basic oxide constituents which rapidly plugged the superheater passages after about 4 h of operation as shown in Figure 13.

Figure 14 shows that the chloride concentrations in ash deposited on furnace walls, superheater tubes and in precipitator hoppers increased by about an order of magnitude to about 10,000 ppm when calcium chloride was added to the limestone or dolomite. Since ash deposits containing high chloride levels are known to cause severe fireside corrosion of high- and low-temperature metal heat exchange surfaces, the use of calcium chloride as an anti-freeze agent for coal should be thoroughly evaluated to identify potentially unacceptable risks to equipment downstream of the pulverizers(4).

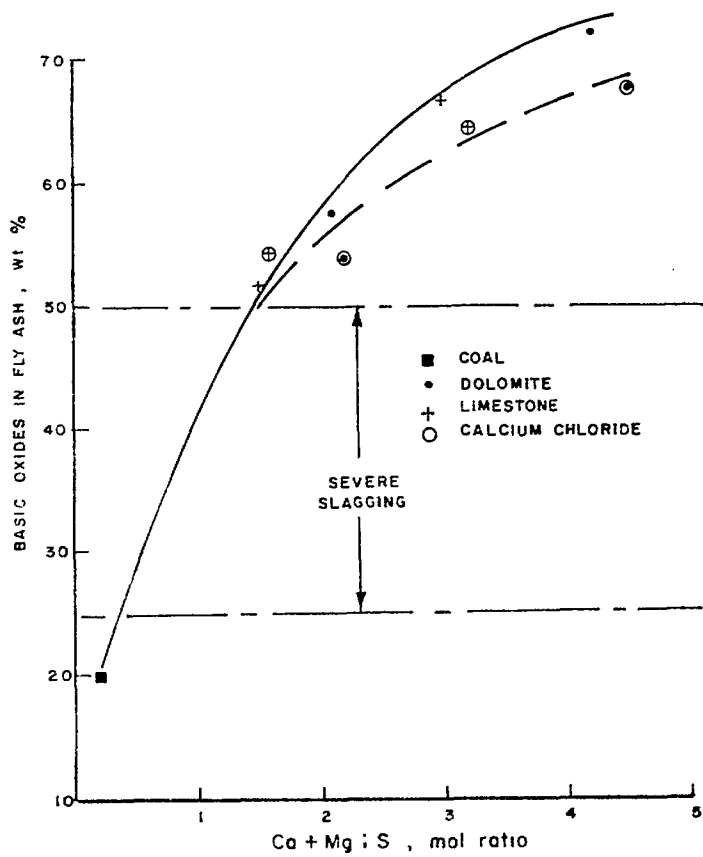


FIGURE 7. Increase in basic oxides in fly ash due to additive treatment.

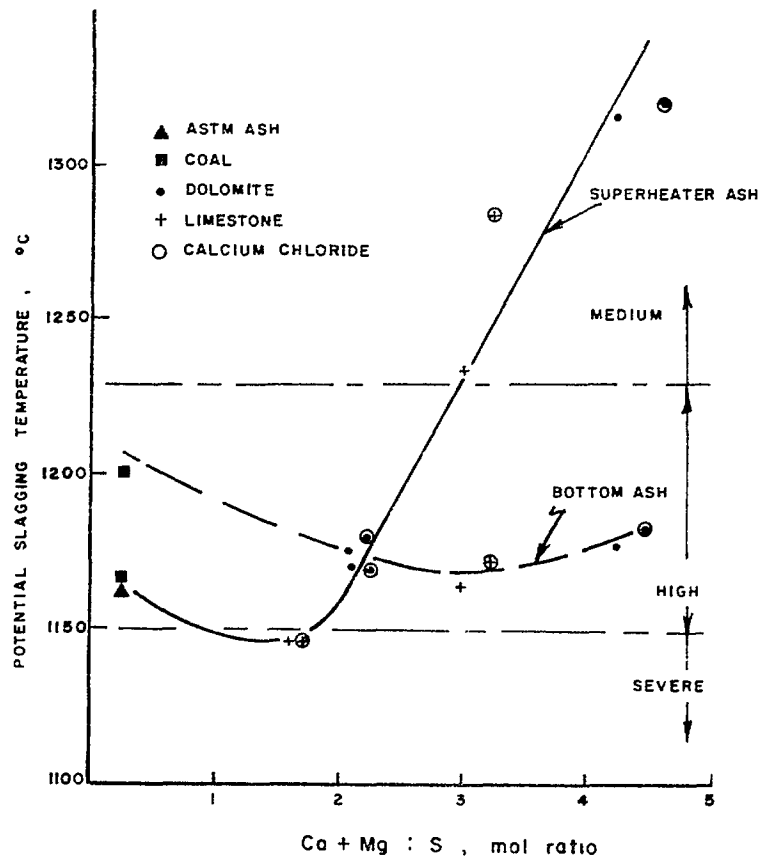


FIGURE 8. Increase in potential slagging temperature of ash deposits due to additive treatment.

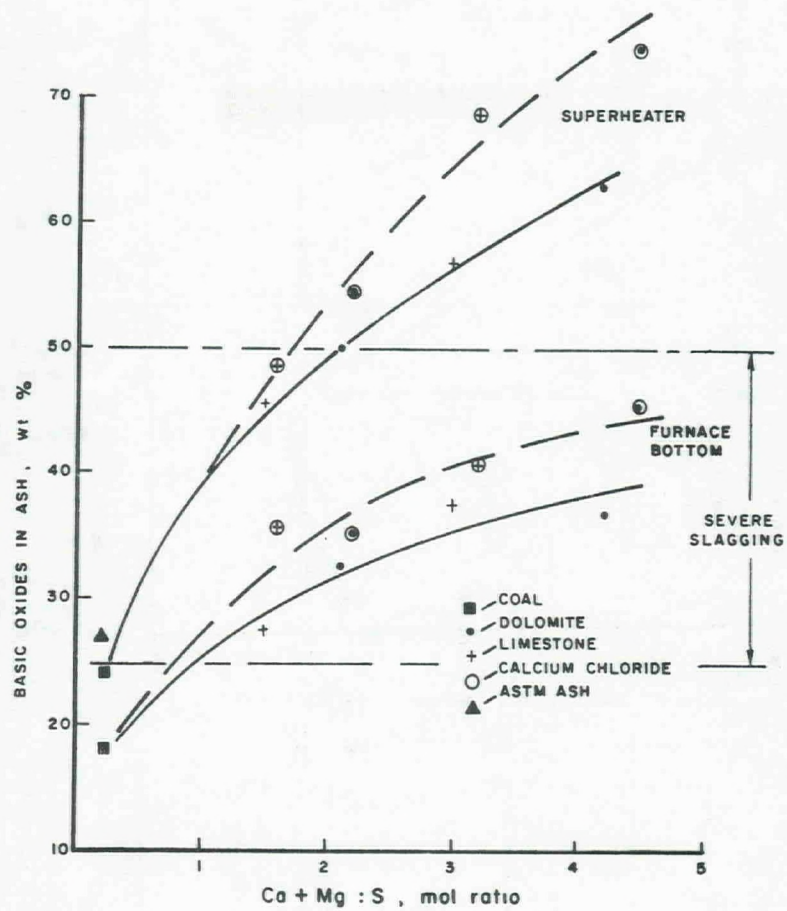


FIGURE 9. Increase in basic oxides in ash deposits due to additive treatment.



FIGURE 10. Slag from furnace bottom.

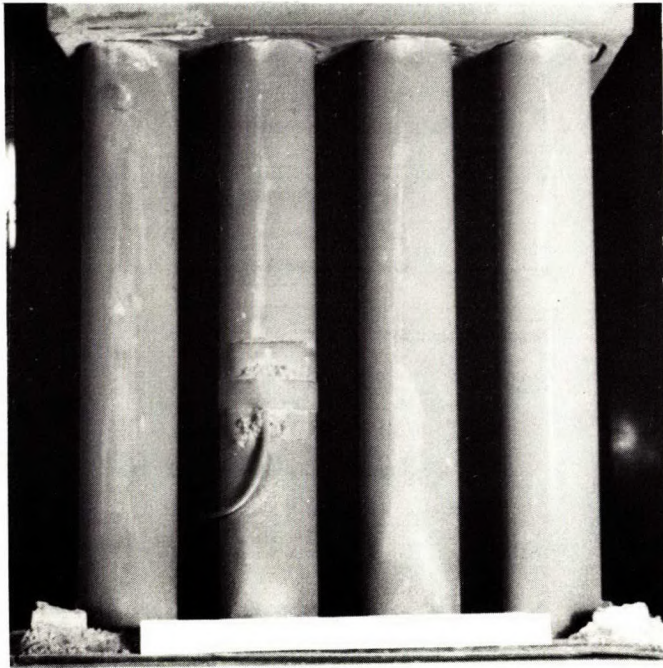


FIGURE 11. Superheater deposits from coal only.

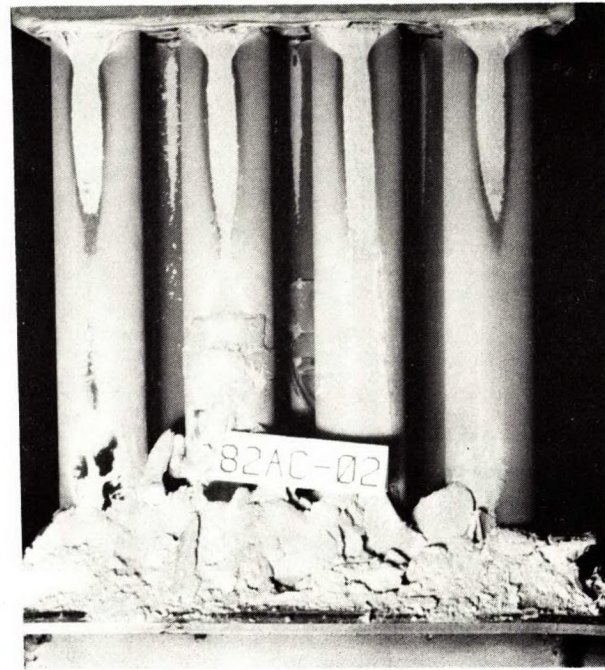


FIGURE 12. Superheater deposits from dolomite addition to coal ($\text{Ca} + \text{Mg}:\text{S} = 4.2$)



FIGURE 13. Superheater blockage due to chloride addition to dolomite and coal ($\text{Ca} + \text{Mg}:\text{S} = 4.5$).

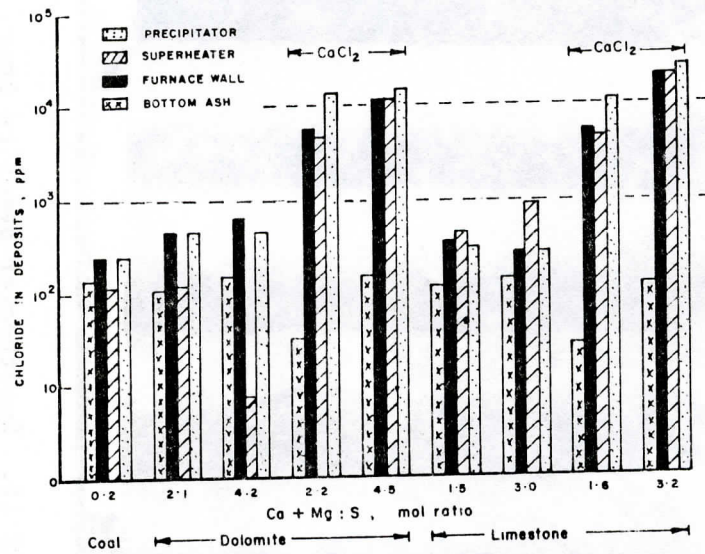


FIGURE 14. Chloride retention in ash deposits.

CONCLUSIONS

1. Sulphur oxide emissions decreased linearly by about 22% and 40% for (Ca + Mg) /S ratios of 2 and 4, respectively using limestone or dolomite as sorbents.
2. Calcium chloride additions to the sorbents improved sulphur retention to 40% and 77% at (Ca + Mg) /S ratios of 2 and 4, respectively.
3. Increased chloride emissions more than offset the incremental sulphur reduction produced by the addition of calcium chloride to the sorbents.
4. The two sorbents, with or without calcium chloride additions, had no effect on NO_x emissions.
5. Calcium chloride retention in fly ash caused accelerated fouling of superheater surfaces and reduced fly ash emissions.
6. Calcium chloride treatment increased the chloride content of dry ash deposits by more than a factor of 10, but had no effect on chloride retention in furnace slag.
7. Although not evaluated during these trials, high chloride levels in coal may accelerate corrosion of boiler metal surfaces.

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