



DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*PAPER 4. EFFECT OF FUEL
CHARACTERISTICS AND EXCESS
COMBUSTION AIR ON SULPHURIC
ACID FORMATION IN A
PULVERIZED-COAL-FIRED BOILER*

G. K. LEE, F. D. FRIEDRICH AND E. R. MITCHELL

Dept. Energy, Mines & Resources
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AUG 15 1967 ✓

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Presented at the Symposium on the
Science and Technology of Coal,
Ottawa, Canada, March 31, 1967



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ROGER DUHAMEL, F.R.S.C.

Queen's Printer and Controller of Stationery

Ottawa, Canada

1967.

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This paper describes part of a continuing research programme aimed at establishing the influence of various factors on the corrosion potential of boiler flue gases. These factors include the sulphur content of coal, the cation content of coal ash and excess combustion air. From the experiments which were conducted in a pilot-scale research boiler with coals containing 6 and 7 per cent sulphur it has been established that SO_3 concentrations, acid dew-point, rate of acid build-up and neutralization of acid by fly-ash all influence corrosion potential; the method for determining the last parameter is described in detail. The findings, so far, strongly suggest that equilibrium data relating only acid concentration and theoretical acid dew-point cannot be applied to the corrosion rate under dynamic boiler conditions where flue-gas constituents such as SO_3 , H_2O and fly-ash are continually deposited from the gas stream. As could be expected, corrosion potential is minimal or non-existent at less than 1 per cent oxygen in the flue gas but high above 3 per cent oxygen.

1. Introduction

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At the time of writing, tests were completed on two coals having sulphur contents of about 6 and 7 per cent respectively, and for comparative purposes some tests were carried out on a lignite containing less than 0.5 per cent sulphur. In these tests, excess O_2 in the flue gases was varied stepwise from 0.5 to 5 per cent.

In a continuation of the research programme coals with sulphur contents ranging from about 3 to 12 per cent, and coals having different ash compositions will be included. At the same time sulphur-neutralizing additives will be evaluated.

2. Description of combustion research boiler

The combustion research boiler, shown diagrammatically in Fig. 1, is a pilot-scale pulverized-coal-fired boiler with a slag-tap furnace and a full-load firing rate of about 200 lb/h of bituminous coal, which corresponds to a steaming rate of about 1 600 lb/h at 15 p.s.i.g. The firing system is composed of two industrial-type opposed burners tilted downward over a refractory-lined slagging chamber. The furnace is of membrane-wall construction, and has a heat release rate of about 75 000 Btu/ft³. The steam generated is dissipated in an air-cooled condenser.

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up to 450°F, or with a mixture of air and flue gas at any temperature up to 800°F. A motor-driven variable-speed classifier built into the pulverizer provides good control of coal fineness. A simple splitting device at the pulverizer outlet divides the coal between two transport pipes, one to each burner. Secondary air can be supplied to the burners at any temperature up to 400°F. The furnace operates at a pressure of about 5 in w.g.

Combustion gases leave the furnace at between 1 400° and 1 600°F, pass through a transition piece, then travel across the tubes of a test air-heater. This air-heater contains 16 interchangeable stainless steel tubes and it was incorporated into the rig design to facilitate future studies of high-temperature corrosion. Finally, the combustion gases pass through the tubes of a three-pass conventional air-heater and enter the stack at a temperature of 500°F or more.

A forced-draught fan supplies air to the main air-heater at a pressure of 26 in w.g. The air leaving the main air-heater is split into three streams: primary air to the pulverizer, secondary air to the burners and cooling air to the test air-heater. The last stream, on leaving the test air-heater, can be directed either to the atmosphere or into the primary-air stream to the pulverizer mill.

The research boiler is manually controlled except for some electrical interlocks to ensure that the correct start-up and safety shut-down procedure is followed. It has been found possible to operate with as little as 0.3 per cent O_2 in the flue gases, having less than 0.1 per cent CO and a smoke density of less than No. 1 Ringelmann, as measured by a self-standardizing light beam type of smoke meter. However, it has been found difficult to hold O_2 in the flue gas constant in the range from 3.5 to 5 per cent O_2 , and the gas-side pressure drop through the air-heaters limits operation at full load to no more than 5 per cent O_2 in the flue gases.

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Three coals have been used in the tests to date: a high-volatile A bituminous from Broughton, Nova Scotia, known as Four Star, a high-volatile A bituminous from Minto, New Brunswick, known as Avon (Minto) and a low-sulphur lignite from Estevan, Saskatchewan. The two bituminous coals from eastern Canada are high in sulphur content and, having low ash-fusion temperatures, they slagged readily in the research furnace. The lignite was burnt for comparative purposes only because of its low sulphur content. It also has a low ash-fusion temperature, but because of its high inherent moisture, furnace temperatures were too low to maintain slag tapping.

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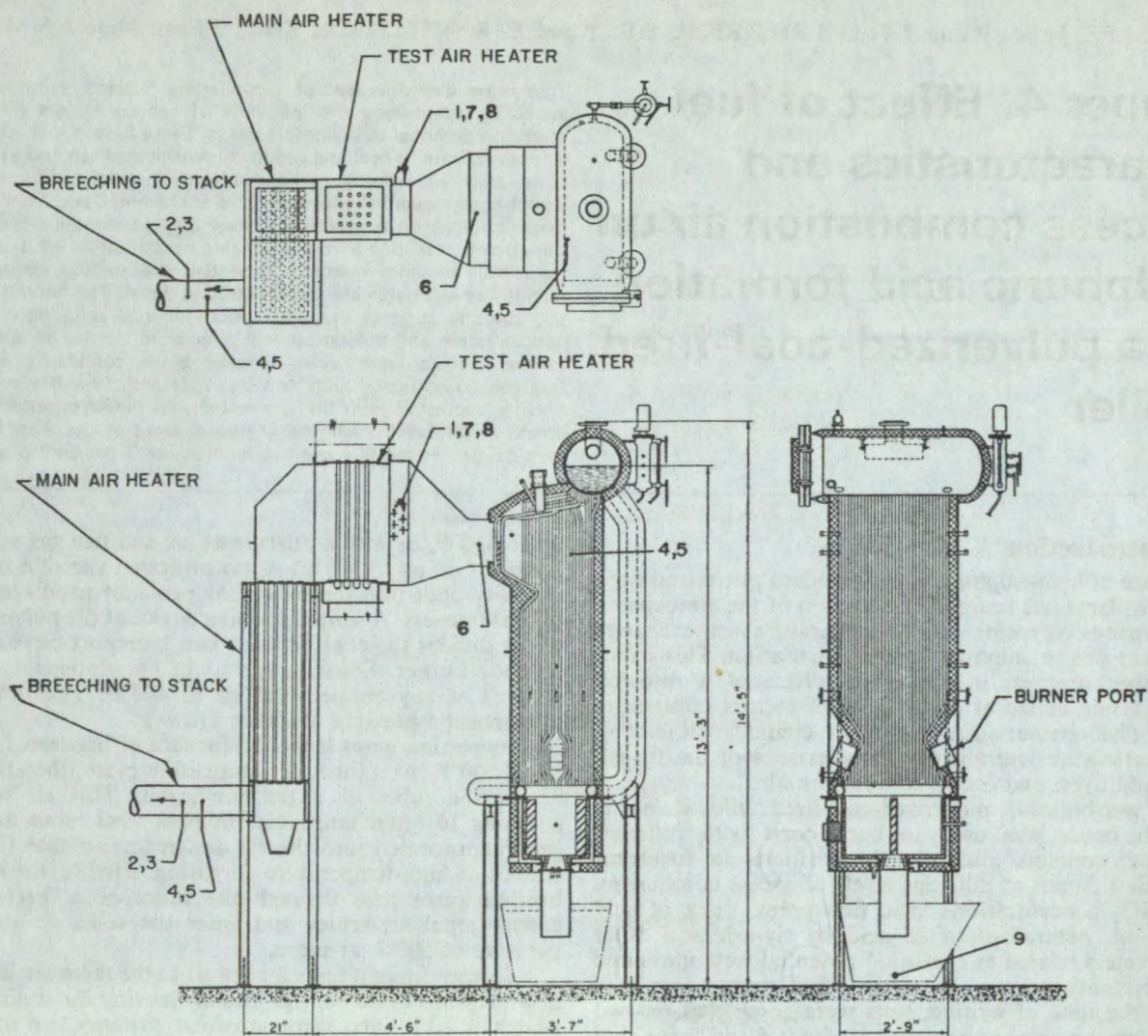


FIG. 1 Schematic diagram of the combustion research boiler showing the sampling locations.

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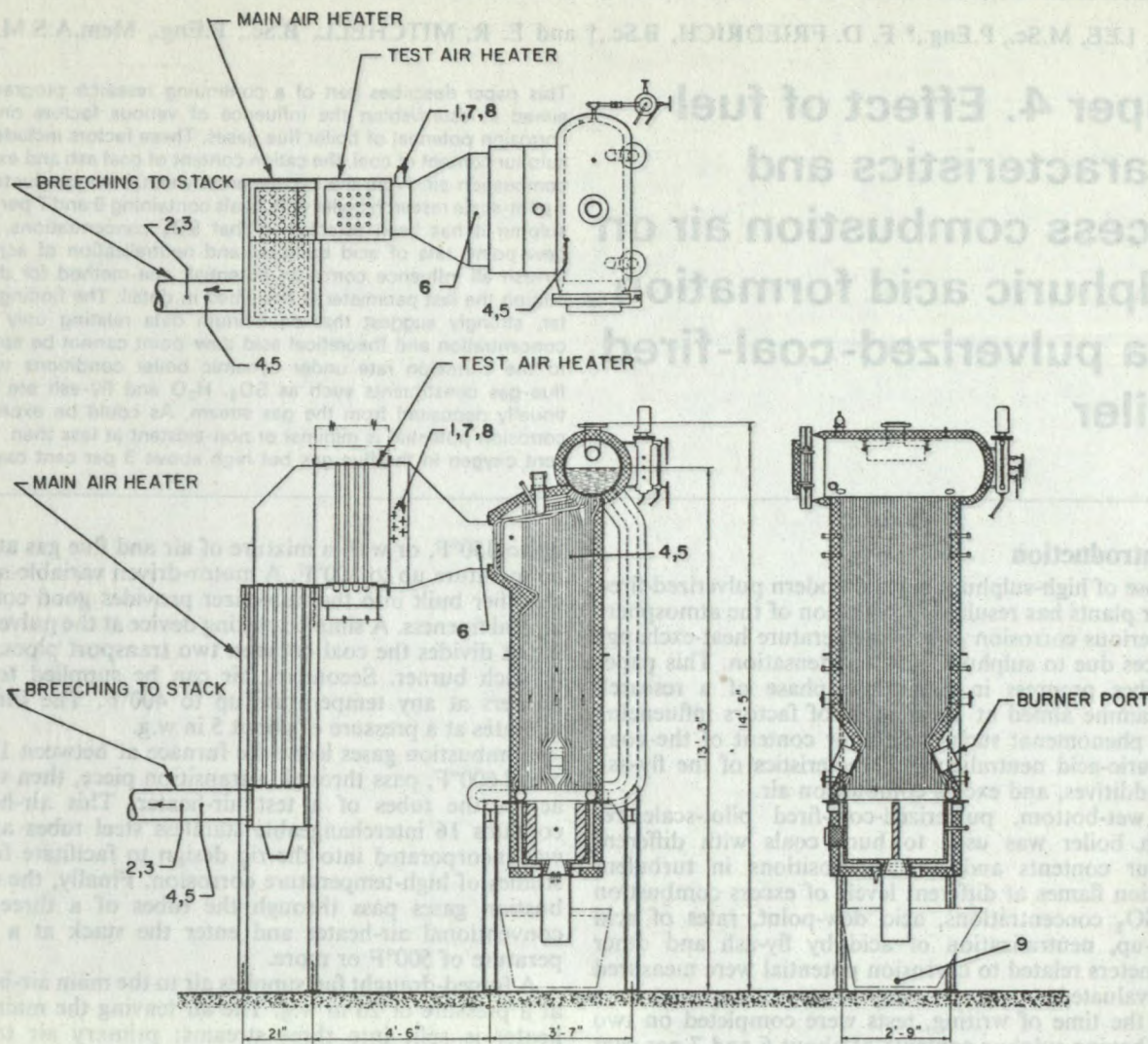


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TABLE 1 Analytical data for the coals tested

	Four Star		Minto		Lignite	
	As rec'd	Dry	As rec'd	Dry	As rec'd	Dry
Proximate analysis, %						
Moisture	1.63	0.00	1.63	0.00	35.85	0.00
Ash	13.53	13.75	17.49	17.78	6.24	9.73
Volatile matter	34.46	35.03	32.44	32.98	27.11	42.26
Fixed carbon (by diff.)	50.38	51.22	48.44	49.24	30.80	48.01
Ultimate analysis, %						
Carbon	67.85	68.97	65.90	66.99	43.45	67.74
Hydrogen	4.50	4.57	4.46	4.53	2.75	4.29
Sulphur	6.20	6.30	7.15	7.27	0.44	0.68
Nitrogen	1.02	1.04	0.71	0.72	0.73	1.14
Ash	13.53	13.75	17.49	17.78	6.24	9.73
Oxygen	5.27	5.37	2.66	2.71	10.54	16.42
Gross calorific value, Btu/lb	12180	12390	12000	12200	7110	11080
Fusibility of ash, °F						
	Reducing	Oxidizing	Reducing	Oxidizing	Reducing	Oxidizing
Initial deformation	1920	2290	1880	1860	1870	1910
Softening, spherical	1990	2450	1950	2430	2050	2260
Softening, hemispherical	2080	2480	2000	2440	2110	2280
Fluid	2200	2530	2160	2450	2150	2300
Ash analysis, %						
SiO ₂		29.97		30.83		24.09
Al ₂ O ₃		18.42		13.46		28.03
Fe ₂ O ₃		35.49		45.62		4.64
TiO ₂		0.50		N.D.		0.87
P ₂ O ₅		0.54		N.D.		0.74
CaO		2.94		2.66		22.61
MgO		1.11		0.50		4.23
SO ₃		3.21		2.11		14.58
Na ₂ O		0.39		0.73	} 0.21	
K ₂ O		2.06		1.77		

Coulter counter, determination of combustible matter and water solubility, and chemical analysis of the residue and the water extract. This measurement did not establish the dust loading.

7. H₂SO₄ deposited in presence of fly-ash at different temperatures below the acid dew-point, by means of a technique described in the Appendix to this paper, up to 4 measurements per run.

8. SO₂ + SO₃ in unfiltered gases. This was measured by means similar to API Method 774-54, and was connected in series with the apparatus described under Test No. 7 above, hence it measured the SO₂ plus any SO₃ that was not condensed in this apparatus. The fact that the particulate matter was not filtered out permitted the neutralizing effect of the fly-ash to be assessed by a comparison of these results with those obtained using filters.

9. Weight of ash slagged in each run. As the weight and ash content of the coal burnt were known, the weighing of the slagged ash made possible a rough calculation of the dust loading in the flue gases. This was done with the Minto coal only.

4.3. Sampling locations

The locations from which the various samples were drawn are shown in Fig. 1. The numbers in the figure correspond to the test numbers used in the section entitled 'Test measurements.' It will be noticed that SO₂ and SO₃ measurements (Nos. 4 and 5) were taken in two locations: near the furnace exit and in the breeching to the stack. Samples were taken from both locations during each run to establish whether the SO₃ level increased through the air-heaters.

5. Test results

5.1. SO₃ versus O₂

SO₃ versus O₂ is plotted in Figs. 2 and 3 for Four Star coal and Minto coal respectively. In these figures each horizontal line represents a measurement. The position of a line relative to the ordinate defines the SO₃ concentration while the length of the line spans on the abscissa the variation in O₂ content of the flue gases during the time in which the sample was drawn. The solid part of each curve was plotted using an electronic computer to average the measured data according to the method of least squares. It was assumed that the test results which had the least variation in O₂ were the most accurate. Accordingly the results were weighted as follows:

Variation in % O ₂	Weighting factor
0.1	4
0.2 to 0.4	3
0.5 to 0.9	2
1.0+	1

The SO₃ curve calculated by the computer for Four Star coal reaches a peak at 5 per cent O₂. It appears that SO₃ does not increase with O₂ beyond this point. However, if the absolute amount of SO₃ remains constant beyond 5 per cent O₂, the relative proportion of SO₃ must decrease by dilution. The dotted portion of the curve in Fig. 2 was plotted by calculating the dilution factor.

With Minto coal the SO₃ curve does not reach a peak within the limits of the measured data. The dotted portion of the curve was plotted by assuming a peak in

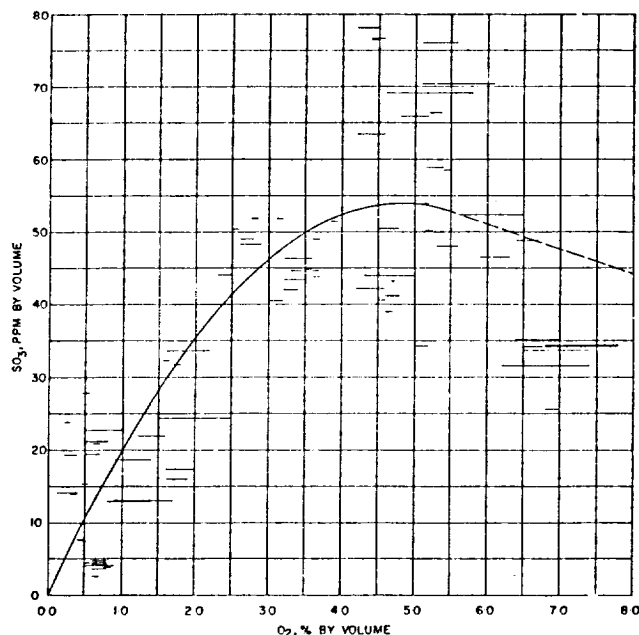


FIG. 2 SO_3 concentration plotted against O_2 in flue gas for Four Star coal.

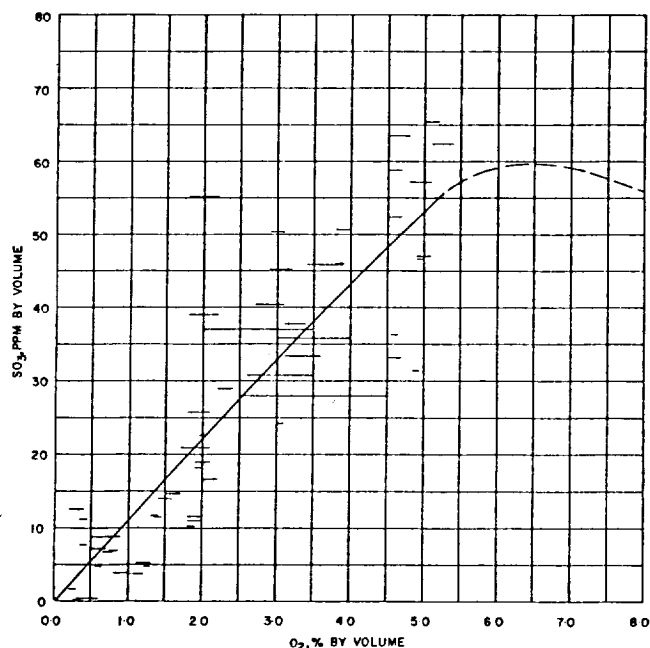


FIG. 3 SO_3 concentration plotted against O_2 in flue gas for Minto coal, 7 per cent sulphur.

the vicinity of 6.5 per cent O_2 , and then calculating a dilution factor as before.

Spot-check measurements during operation with lignite showed that virtually no SO_3 was formed at any oxygen level. None of the coals tested showed any significant change in SO_3 concentration between the furnace outlet and the stack.

5.2. Acid dew-point temperature and maximum rate of acid build-up

Acid dew-point temperature and maximum RBU are plotted in Figs. 4 and 5 for Four Star coal, and in Figs. 6 and 7 for Minto coal. Four Star coal shows a maximum acid dew-point temperature of 285°F at 5 per cent O_2 , while Minto coal shows a maximum dew-point of 295°F at about 3 per cent O_2 . Both coals show a maximum rate of acid build-up of about $800 \mu\text{A}/\text{min}$,*

* $\mu\text{A}/\text{min}$ = micro-amperes/minute.

but with Four Star coal the peak occurs at 5 per cent O_2 , while with Minto coal the peak occurs at between 3 and 4 per cent O_2 . The dotted portions of the curves represent the effect of dilution as previously explained.

With lignite, a dew-point temperature of 105°F was measured. Obviously this was the water dew-point and it was meaningless to attempt to establish rates of acid build-up.

It is noteworthy that in the case of Four Star coal the maximum acid dew-point temperature, the maximum RBU and the maximum SO_3 level all occur at the same O_2 level, namely about 5 per cent. In the case of Minto coal acid dew-point temperature and RBU reach a maximum at about 3 and 4 per cent O_2 respectively, while SO_3 reaches a maximum at somewhere in excess of 5 per cent O_2 .

In Fig. 8 the measured correlations between SO_3 concentration and acid dew-point temperature are compared with the theoretical correlation calculated by Mueller.¹ Whittingham's correlation measured on a Bunsen burner flame is also included. There appears to be no agreement between the calculated and the measured data.

5.3. Suppression of SO_3 by fly-ash and corrosion potential of flue gas

The suppression of SO_3 by pulverized-coal fly-ash, carbon smoke and inorganic dusts has been the subject of much research, particularly in Great Britain^{3,4} and Denmark.⁵ Accordingly, two series of experiments were conducted to assess the role of fly-ash in (a) reducing SO_3 in the flue gas, and (b) neutralizing the corrosiveness of SO_3 that condenses on surfaces below the acid dew-point. These experiments were carried out during the combustion tests with Minto coal at mean oxygen levels of 0.5, 1.5, 3 and 4.5 per cent.

5.3.1. Reduction of SO_3 by fly-ash

In this series of experiments representative samples of

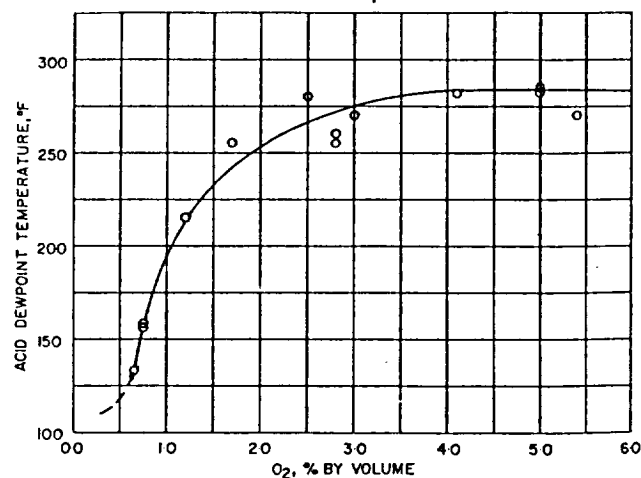


FIG. 4 Acid dew-point temperature plotted against O_2 in flue gas for Four Star coal.

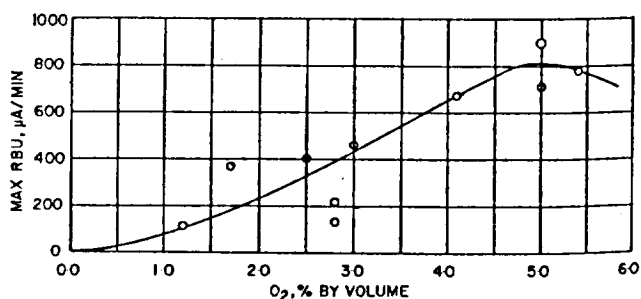


FIG. 5 Maximum rate of acid build-up plotted against O_2 in flue gas for Four Star coal.

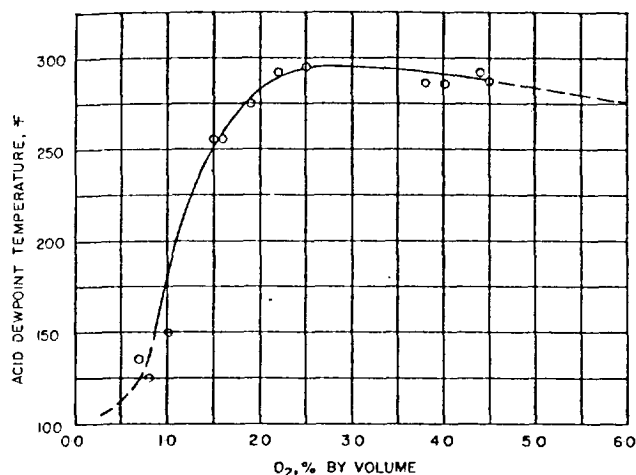


FIG. 6 Acid dew-point temperature plotted against O_2 in flue gas for Minto coal, 7 per cent sulphur.

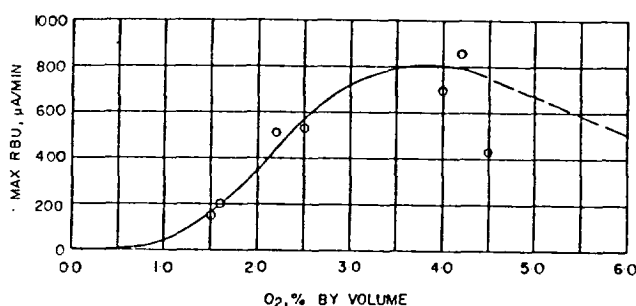


FIG. 7 Maximum rate of acid build-up plotted against O_2 in flue gas for Minto coal, 7 per cent sulphur.

fly-ash were withdrawn from the gas stream at location 6 (see Fig. 1) at temperatures above the acid dew-point. Typical analyses of these samples, given in Table 2, show that the water solubility of the fly-ash increased with the oxygen content of the flue gas and that the water extracts contained mostly calcium, magnesium, iron and sulphate. Although all the water extracts had a cation deficiency, their pH values indicated that no free sulphuric acid was

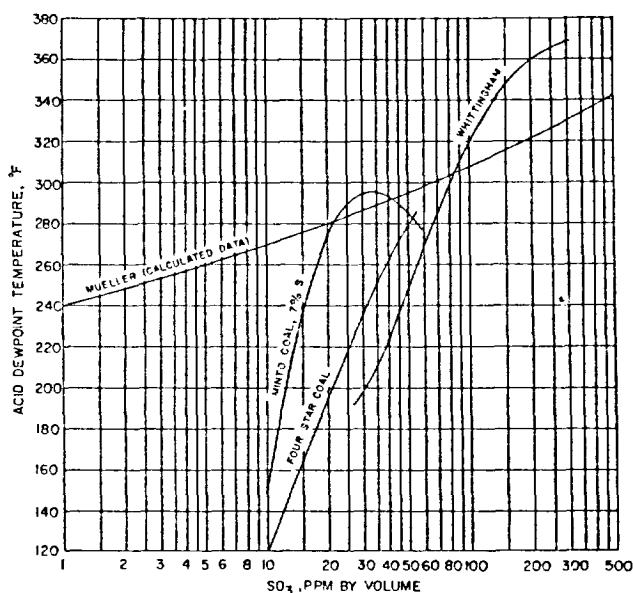


FIG. 8 Acid dew-point temperature plotted against SO_3 concentration in flue gas.

present in the fly-ash with 0.5 per cent oxygen in the flue gas. However, as the oxygen level of the flue gases was progressively increased to 1.5, 3 and 4.5 per cent, the water extract increased correspondingly in both free sulphuric acid and reaction products of sulphate, calcium, magnesium and iron. The comparatively large amounts of water-soluble iron formed during the tests at 3 and 4.5 per cent oxygen suggest that iron in the fly-ash partially neutralizes the increase in SO_3 generated by high excess combustion air. Analyses of the water extracts also indicate that increases in fly-ash solubility are associated with increases in SO_3 content and that the alkaline earth elements, calcium and magnesium, together with iron are better neutralizers and adsorbers of sulphuric acid vapour than sodium or potassium. It is, therefore, evident that the insoluble alkali elements in the fly-ash are combined in a mineral form that does not readily react with sulphuric acid vapour.

TABLE 2 Chemical analyses of fly-ash samples extracted from flue gases during combustion of Minto coal

Mean oxygen level in flue gas	0.5%		1.5%		3%		4.5%	
Ash composition, %	Water extract	Residue	Water extract	Residue	Water extract	Residue	Water extract	Residue
SiO_2	—	22.43	—	28.60	—	27.54	—	31.01
Al_2O_3	Trace	10.05	Trace	12.46	Trace	12.47	Trace	13.28
Fe_2O_3	<0.01	29.15	<0.01	34.47	0.17	30.81	0.85	31.33
CaO	0.46	1.37	0.61	1.12	0.85	1.10	0.59	1.23
MgO	0.03	0.34	0.02	0.74	0.06	0.74	0.07	0.79
SO_3	0.63	0.53	0.87	0.45	1.45	0.23	2.01	0.38
Na_2O	0.01	0.65	0.01	2.07	0.02	0.38	0.02	0.93
K_2O	0.01	1.29	0.01	1.57	0.02	1.61	0.02	1.84
Solubility	1.41		1.76		3.12		4.30	
pH*	7.4		6.4		4.7		4.7	
Soluble sulphate	2.05		1.94		2.20		2.27	
Soluble cation								
Combustible	31.3		16.1		18.6		12.3	
Particle size distribution	Total sample		Total sample		Total sample		Total sample	
+ 149	4.2		7.1		7.8		24.7	
74 × 149	12.3		23.7		26.6		28.3	
37 × 74	30.4		21.2		27.9		19.9	
10 × 37	45.7		35.8		32.2		20.6	
0 × 10	7.4		12.2		5.5		6.5	

*Extract from 1 g of deposit in 100 ml distilled water.

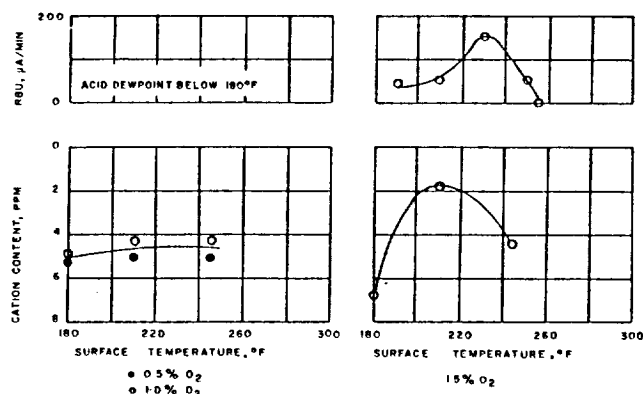


FIG. 9 Variation in rate of acid build-up and cation content of fly-ash with surface temperature. Minto coal (7 per cent sulphur) with low excess air.

Microscopic examination and particle-size analyses of the fly-ash revealed that increases in the weight of minus 37 micron particulates, resulting from decreases in excess combustion air, were mostly due to coke cenospheres rather than carbon smoke.

Generally it was found that reductions in oxygen content of the flue gases not only increased the combustible in the fly-ash but reduced both the SO_3 content of the flue gas and the water-soluble sulphate in the fly-ash. It is known that low excess-combustion air prevents the formation of SO_3 ^{6,7} and that coke particles are capable of chemically reducing SO_3 to SO_2 ^{8,9}. Nonetheless, the absence of free sulphuric acid in fly-ash produced with 0.5 per cent oxygen in the flue gas indicates that even relatively high amounts of combustible (coke) in the flue gas are ineffective in physically adsorbing SO_3 . Reductions in SO_3 at a given oxygen level are therefore controlled primarily by chemical reactions with calcium, magnesium and iron and by physical adsorption by inorganic particles of fly-ash. The latter process is assumed because fly-ash samples collected above the acid dew-point contained free sulphuric acid.

5.3.2. Neutralization of condensed sulphuric acid by fly-ash

To clarify the role of fly-ash in neutralizing condensed sulphuric acid an experimental technique* was evolved whereby dust-laden flue gases are drawn through a condensing chamber controlled at a pre-selected temperature below the acid dew-point. Thus samples of fly-ash are collected in the presence of condensed sulphuric acid. By collecting successive samples at condensing-chamber temperatures of 275°, 245°, 212° and 180°F respectively, it was found that increases in the concentration of acid-neutralizing cations (Ca, Mg and Fe) in the fly-ash and decreases in rate of acid build-up can be related to the reduction in excess combustion air. These trends are evident from Figs. 9 and 10 which also show that the curves for both cation concentration and rate of acid build-up versus surface temperature are similar in shape. If one refers to the lower curves in Fig. 10, it is significant that the cations in the fly-ash are not only totally neutralized but contained free acid when acid condenses between 180° and 230°F. In practical terms this means that at oxygen levels above 3 per cent the fly-ash is wet and sticky due to high rates of acid build-up. It follows that corrosion will occur on low-temperature heat-transfer surfaces during both boiler ON and OFF cycles.

According to Niepenberg¹⁰ high corrosion rates are experienced in oil-fired boilers when mild steel surfaces

are maintained at temperatures corresponding to rates of acid build-up in excess of 100 $\mu\text{A}/\text{min}$. Furthermore, Black *et al.*¹¹ imply that this rate may be increased by a factor of two (200 $\mu\text{A}/\text{min}$) for the same corrosive effect in pulverized-coal-fired boilers because of the acid-neutralizing properties of fly-ash. These observations in conjunction with the data presented in Fig. 10 indicate that boiler heat-transfer surfaces must be maintained above the acid dew-point to prevent catastrophic corrosion when Minto coal is burnt with more than 3 per cent oxygen in the flue gases.

It should be mentioned that corrosion may well occur even when there are sufficient cationic constituents in deposits of fly-ash to neutralize entirely any free acid. Such a condition will exist if part of the condensed acid reacts preferentially with steel boiler surfaces rather than acid-neutralizing matter in the fly-ash. Experiments to study the corrosion of mild steel in the presence of deposited fly-ash and condensed acid will be conducted later in the programme.

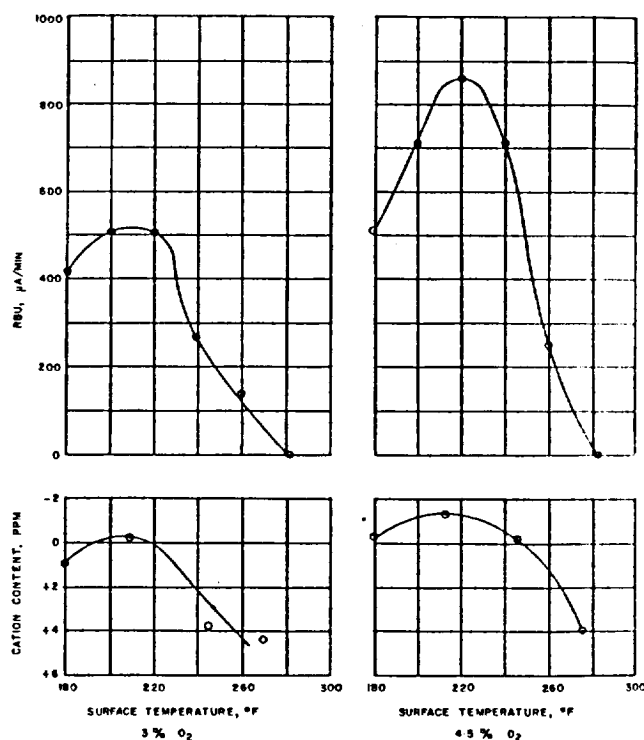


FIG. 10 Variation in rate of acid build-up and cation content of fly-ash with surface temperature. Minto coal (7 per cent sulphur) with normal excess air.

5.4. Slag analyses and refuse balance

Samples of slag representing each coal at various levels of excess oxygen during combustion were drawn from the quenching tank and submitted to chemical analysis and ash fusion determinations. Some typical results are given in Table 3.

A rough ash balance was computed for Minto coal, and it indicates that about 40 per cent of the ash was collected as slag. The remainder presumably passed through the boiler as fly-ash.

6. Conclusions

1. When burning coal with more than 5 per cent sulphur, there appears to be no relationship between:

- SO_3 level in the flue gases and sulphur content of the coal,
- SO_3 level and acid dew-point,
- SO_3 level and corrosion potential as measured by rate of acid build-up,

*See Appendix for details of sampling procedure.

TABLE 3 Typical analyses and ash fusion data for slags from the coals tested

Coal	Lignite Four Star			Minto	
Excess O ₂ during combustion, %	3.5	0.5	3.3	1.0	4.5
Slag analysis, %					
SiO ₂	37.27	30.57	30.00	35.33	35.50
Al ₂ O ₃	17.21	26.12	17.24	15.32	15.04
Fe ₂ O ₃	11.53	35.68	39.96	39.96	40.18
TiO ₂	0.61	0.62	N.D.	N.D.	N.D.
P ₂ O ₅	0.59	0.45	N.D.	N.D.	N.D.
CaO	17.99	2.66	2.24	1.75	1.61
MgO	4.58	0.60	1.36	1.16	1.06
SO ₃	2.47	0.97	0.90	1.07	1.03
Na ₂ O	8.48	0.58	0.73	0.48	0.58
K ₂ O	0.00	1.91	2.17	1.99	2.06
Ash fusibility, °F					
Reducing conditions					
Initial deformation	1760	—	—	1860	1860
Softening, spherical	1880	—	—	1890	1940
Softening, hemispherical	1950	—	—	1920	1960
Fluid	2080	—	—	2080	2050
Oxidizing conditions					
Initial deformation	—	—	—	2280	2280
Softening, spherical	—	—	—	2490	2500
Softening, hemispherical	—	—	—	2510	2510
Fluid	—	—	—	2520	2520

(d) measured values of SO₃ and acid dew-point as compared with values calculated from equilibrium data.

2. SO₃ levels and acid dew-point temperatures reach a peak somewhere between 3 and 6 per cent O₂ in the flue gases.

3. Partial neutralization of SO₃ in flue gases occurs through both chemical reaction with calcium, magnesium and iron and physical adsorption by inorganic particulates in fly-ash.

4. Corrosion potential as measured by increasing rates of acid build-up can be inversely related to the concentration of acid-neutralizing cations in the fly-ash. The presence of free sulphuric acid in the fly-ash coincided with rates of acid build-up that are associated with high rates of corrosion.

5. As would be expected, corrosion potential is minimal or non-existent at less than 1 per cent oxygen in the flue gases.

7. Acknowledgments

Valuable assistance was provided by R. G. Fohse and the entire staff of the Canadian Combustion Research Laboratory in the shift operation of the laboratory boiler, in analysing test specimens and in giving general support to the research programme. Thanks are due to W. J. Montgomery and staff of the Solid Fuels Analysis Section for coal and ash analyses. Computer programming was done by N. A. Toews of the Mining Research Laboratories to whom we are indebted for this and other assistance.

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Appendix

A method for determining the degree of neutralization of sulphur oxides by particulate matter in boiler flue gases

Outline of method

The gas containing entrained solids is drawn through a teflon vial immersed in a temperature-controlled glycol bath to collect condensed sulphur trioxide in the presence of particulate matter. The temperature differential between the acid dew-point and that selected for the bath controls the amount of condensed acid available for reaction with cations in the fly-ash. The vial may contain an excess of either condensed SO₃ or cations in the fly-ash. Excess SO₃ is determined volumetrically with standard sodium hydroxide solution while excess cations are determined volumetrically with standard hydrochloric acid solution.

Two bubblers in series containing sodium hydroxide neutralize any sulphur oxides in the effluent from the vial. These sulphur oxides are determined volumetrically with standard hydrochloric acid solution.

Sampling apparatus

The sampling apparatus, illustrated schematically in Fig. 11 incorporates:

(a) A sampling probe of 12 mm i.d. stainless steel or vitreosil which extends to the centre of the sampling zone. If gas temperatures are below 900°F stainless steel may be used but above 900°F either vitreosil or a non-porous refractory tube must be used to prevent catalytic oxidation of SO₂ to SO₃. The exit end of the probe terminates with a $\frac{3}{8}$ in stainless steel tube union.

(b) An SO₃ condenser system (see Fig. 12), consisting of a glycol bath and a 1 to $\frac{1}{4}$ in o.d. \times 3 in long teflon vial fitted with a knurled stainless steel cap. Silver soldered to this cap is (i) a $\frac{3}{8}$ in stainless steel inlet tube approximately 20 in long which extends from the probe union to a point 2 in inside of the vial, and (ii) a $\frac{3}{8}$ in stainless steel outlet tube which extends from the top of the cap to a point about 4 in above the level of glycol in the bath. The end of the outlet tube is connected to

(c) an SO₂ absorption train (see Fig. 12), consisting of two bubblers connected in series. The outlet of the second bubbler terminates in a spray trap that is connected to

(d) a wet-test meter (1 ft³/rev) equipped with a thermometer to measure gas temperature (°F, T_{WTM}) and a manometer to measure pressure drop (Δp). The outlet of the wet-test meter is joined to

(e) the inlet of a vacuum pump capable of drawing gas at a rate of 12 ft³/h. A pump of this capacity is normally sufficient to achieve isokinetic sampling conditions.

(f) Electric heating elements with adjustable thermo-

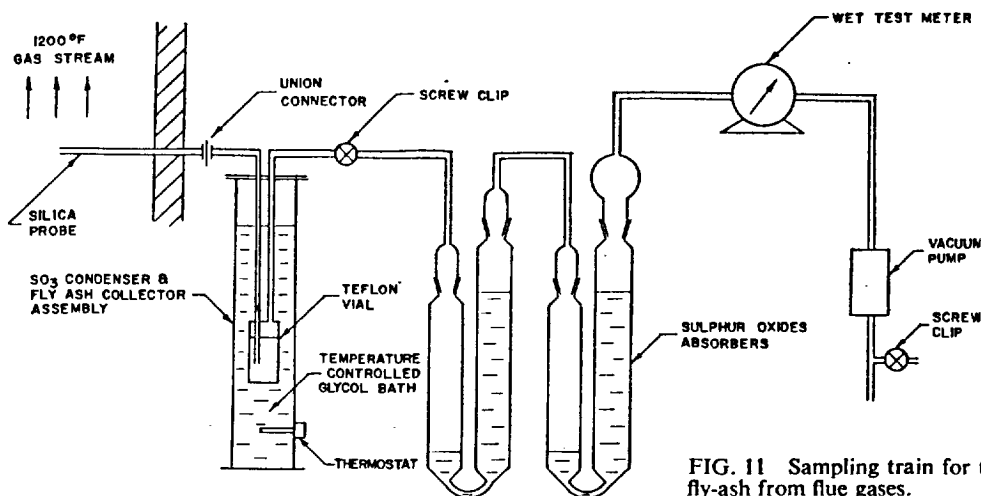


FIG. 11 Sampling train for the extraction of sulphur oxides and fly-ash from flue gases.

stat to control the glycol bath in the condenser unit at the desired temperature, and

(g) A stop watch.

Condenser temperatures

Condenser temperatures for the tests described were controlled by ethylene glycol baths at 180°, 212°, 245° and 275°F. Ethylene glycol has a boiling point of 385°F and bath temperatures of up to 320°F can be maintained without the use of a supplementary vapour trap.

Apparatus for analysis

- (i) 5600-ml beakers with watchglasses
- (ii) 5250-ml " " "
- (iii) large hot plate
- (iv) 100-ml burette
- (v) 5-ml microburette
- (vi) pH meter
- (vii) magnetic stirrer
- (viii) two 2000-ml Guth washing bottles
one 8-oz polyethylene washing bottle.

Reagents

Wherever possible reagents should be of 'Analytical Reagent' quality.

(i) 5 per cent isopropyl washing solution. Adjust the solution where necessary to a pH of 7.0 by adding dilute HCl and back titrate with 0.02N NaOH.

(ii) Sodium hydroxide; 0.2N and 0.02N standardized against standard 0.02N HCl acid with bromophenol blue as indicator.

(iii) Bromophenol blue.

(iv) Hydrochloric acid solution, 0.02N and 0.2N standardized against standard 0.02N NaOH.

(v) Hydrogen peroxide solution, 3 per cent.

Preparation of apparatus for sampling

(a) Ensure that the bath solution in the condenser unit is of sufficient volume to immerse completely the teflon vial. Secure lid of condenser jacket tightly. Check to verify that the pinchcock on the condenser outlet is tightly closed. Adjust thermostat to provide the required bath temperature and switch on electrical heating element. Allow bath to reach constant temperature before sampling.

(b) Ensure that all glassware is chemically clean and dry. Charge each twin-bubbler with 100 ml of 0.2N NaOH and 25 ml of 3 per cent H_2O_2 . Record total volume of 0.2N NaOH used in both bubblers (V_{NaOH}) and normality of NaOH (N_{NaOH}).

Sampling procedure

Assemble the apparatus for sampling as shown in Fig. 11 making certain that all connexions are secure.

Fully open the pinchcock on the condenser unit outlet and turn on the vacuum pump. Adjust the relief valve on pump until the flow rate is 12 ft³/h. Record the following data:

T_{WTM} = temperature of gas at wet-test meter, °F,

P_b = barometric pressure, in Hg,

Δp = drop in pressure across wet-test meter, in Hg.

After sampling approximately 2 ft³ of gas switch off pump, close pinchcock tightly and disassemble sampling train. Record volume of gas sampled (V_{WTM}).

Sample analysis

(i) Vial contents

Using 5 per cent isopropyl solution wash out the contents of the teflon vial into a 250 ml beaker thoroughly. Dilute the wash to 150 ml with isopropyl; cover with watchglass and set on hot plate. Boil for about 30 min. During boiling wash down sides of beaker with small amounts of 5 per cent isopropyl alcohol. Titrate to end point of 7.0 using 0.02N HCl if the pH > 7.0 or 0.02N NaOH if the pH < 7.0.

Record VT_1 = volume (ml) of titrant,

N_1 = normality of titrant.

Filter contents or titrated vial solution through a 1.2 μ millipore disc; dry and weigh the ash residue (M_V).

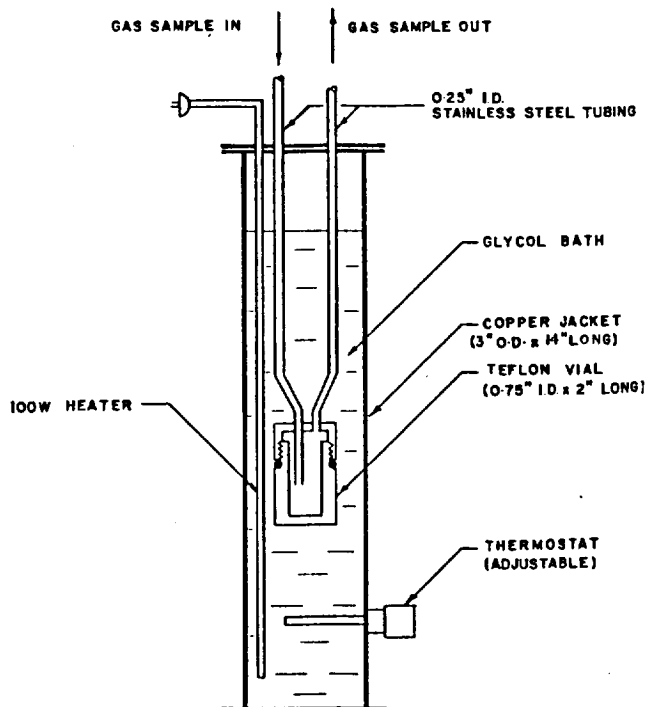


FIG. 12 Sulphur trioxide condenser and fly-ash collector assembly.

(ii) *Bubbler contents*

Pour the contents of both bubblers into a 600-ml beaker. Using distilled water, thoroughly wash out all the connecting tubes and glassware being certain to flush all surfaces exposed to the gases. Bring contents of the beaker to a slow boil and continue heating for about 20 min to eliminate any H_2O_2 . After boiling titrate to end point of 4.5 using 0.2N HCl. Record volume of titrant (VT_2) and normality of titrant (N_2). Filter contents of titrated bubbler solution through a 1.2μ millipore disc; dry and weigh fly-ash (M_B).

Calculation

(i) Correction of volume of gas to $60^\circ F$

(a) adjust V_{WTM} according to calibration factor on wet-test meter,

(b) apply this corrected volume (V_a) to the equation

$$\frac{(V_a)(17.38)(P_b - \Delta_p)}{(T_{WTM} + 460)} = V_{60^\circ}$$

$$(ii) SO_3, \text{ p.p.m.} = \frac{417 (VT_1) (N_1)}{V_{60^\circ}}$$

$$(iii) SO_2, \text{ p.p.m.} = \frac{417 [(ml, NaOH) (N, NaOH) - (VT_2) (N_2)]}{V_{60^\circ}}$$

$$(iv) \text{ g/ft}^3 \text{ fly-ash} = \frac{M_v + M_b}{V_{60^\circ}}$$