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SOME APPLICATIONS OF THE ULTRAMICROBALANCE TO POWER STATION FLUE GAS RESEARCH*

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ABSTRACT

Mechanisms of formation and emission of acid smuts have been investigated using an apparatus based on an ultramicrobalance. Conclusions drawn from the experimental results are that, of the three potentially most significant smut-forming processes, condensation of sulphuric acid is most important whilst catalytic adsorption of sulphur dioxide and sulphuric acid adsorption above the acid dewpoint play minor roles.

INTRODUCTION

Acid smuts are agglomerates of combustion produced solids, mainly carbon, in association with varying amounts of sulphuric acid.

Acid smut emission is seen as an important immediate environmental problem concerning the Central Electricity Generating Board (CEGB). Although emissions are local and spasmodic, rarely if ever causing serious damage, they have a major effect on public relations and planning. Avoidance of these emissions is therefore highly desirable and this requires an understanding of acid smut formation and emission mechanisms.

The residual fuel oils used in oil-fired stations contain, typically, 2 to 4% by weight of sulphur. During combustion this sulphur is converted mainly to sulphur dioxide but a very small amount (a few vppm) of sulphur trioxide is also formed. As flue gases cool during their passage through the boiler to the stack, the sulphur trioxide combines with water vapour present to form sulphuric acid vapour. If back-end surface temperatures are low, e.g., during plant start-up, it is possible for this sulphuric acid vapour to condense on cool surfaces forming a film of liquid acid. Combustion of oil also produces very small amounts of finely divided particles containing unburnt carbonaceous materials. Any of these particles which come into

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contact with acid damp surfaces will accumulate with the result that there is a gradual formation of a solid deposit containing a high concentration of acid. As the surfaces warm up, thermal strains cause this deposit to fracture and flake. A proportion of these flakes will pass through the system and out of the stack, emerging in the atmosphere as acid smuts.

In addition to the acid condensation process described above, there are other ways in which carbonaceous solids and sulphur oxide containing flue gases can be postulated to interact to produce acid smuts. Two processes which could contribute to acid smut formation are oxidation of sulphur dioxide in the presence of flue gas solids and adsorption of sulphuric acid on flue gas solids above the acid condensation temperature (often termed the acid dewpoint).

These three aspects of the problem have been investigated with apparatus based on an ultramicrobalance.

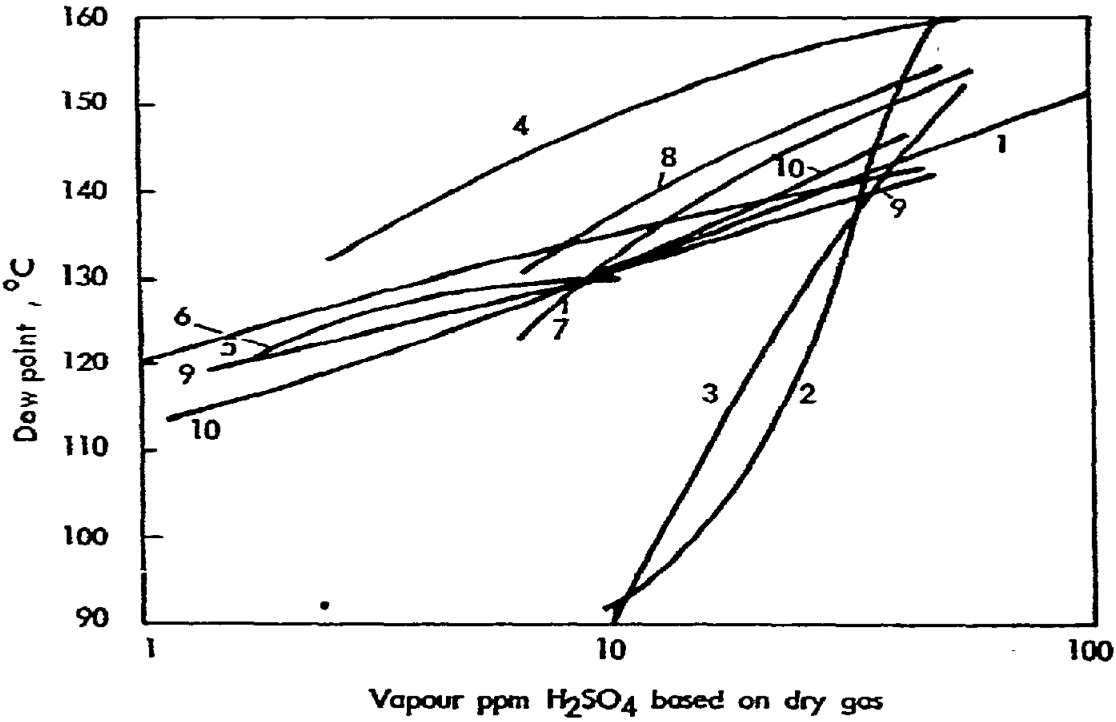

Fig. 1. Experimental dew point curves.

(1)	Evans and Targett,	1975, 10% water (synthetic gas mixture, SG)	
(2)	Dooley and Whittingham,	1946, 15% water (real flue gas, FG)	
(3)	Taylor,	1942, 8.5% water (SG)	
(4)	Rylands and Jenkinson,	1954, 10% water (SG)	
(5)	Francis,	1952, 10% water (product of gas flame)	
(6)	Goksoyr and Ross,	1962, Saturation method (SG)	10%
(7)	Goksoyr and Ross,	1962, Chemical dew point (FG)	
(8)	Goksoyr and Ross,	1962, BCURA dew point meter (FG)	
(9)	Lisle and Sensenbaugh	1965, (filtered flue gas)	
(10)	Lee,	1971, 10% water (SG).	

The importance of the acid dewpoint

The essential information with regard to acid condensation is the relationship between acid dewpoint and gas phase concentration of sulphuric acid. With this

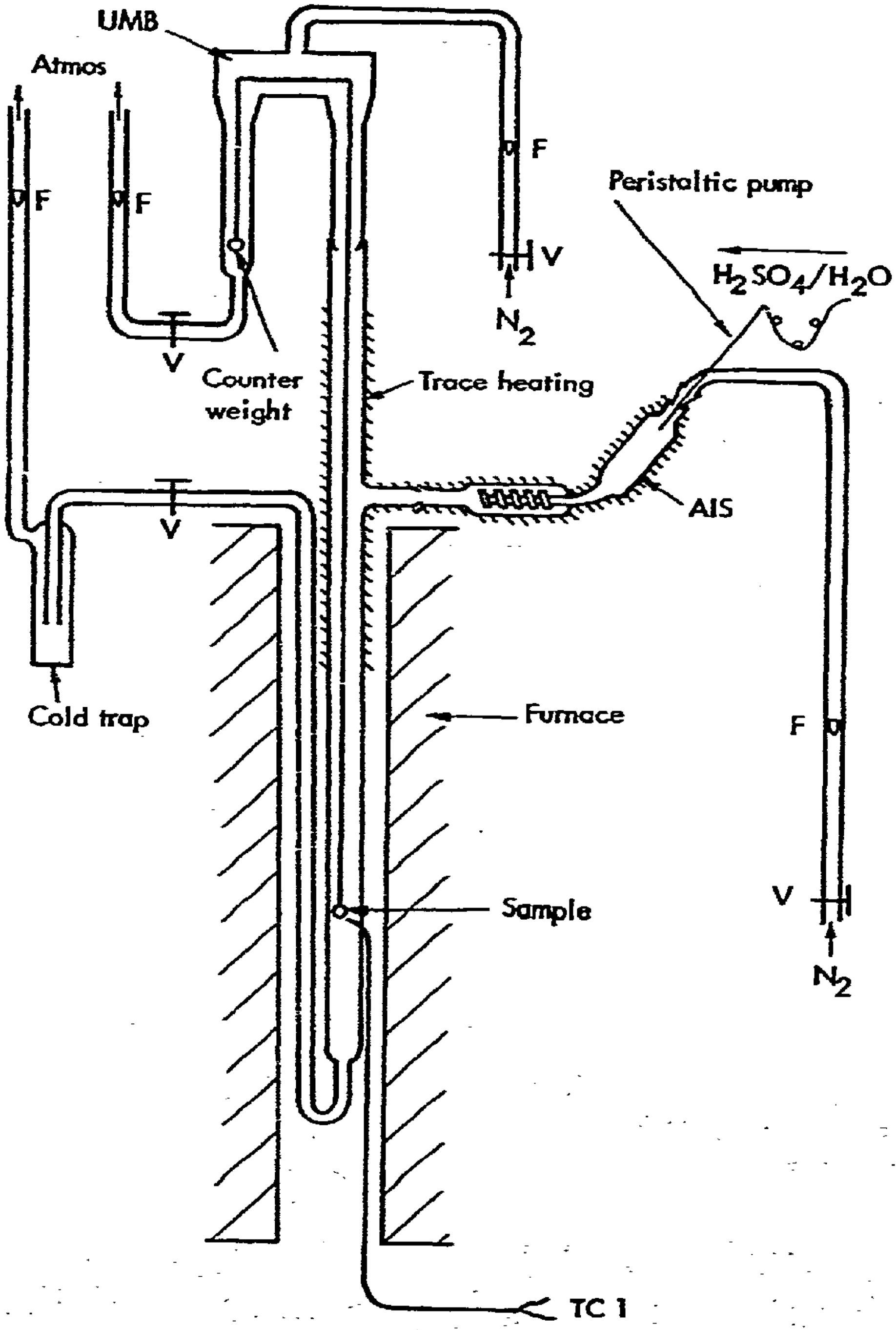

Fig. 2. The apparatus. V = valves; F = flow meters.

information, it is possible to specify the operating conditions necessary to minimise the risk of acid smut formation.

The dewpoint curve can be calculated thermodynamically from vapour pressure data[1, 2]. The direct experimental results show wide variations from the thermodynamic curve, in most cases, and, indeed, amongst themselves (Fig. 1). It has been suggested that this variation may be due to differences in the behaviour of real flue gas as compared with the synthetic mixtures often used. Figure 1 includes examples of both cases and shows that there is no systematic variation consistent with this suggestion.

The recent calculation of the dewpoint curve by Halstead and Talbot[3] uses the best available vapour pressure data and it was of considerable interest to ascertain whether direct measurements by a new technique would confirm this latest thermodynamically derived dewpoint curve. The microgravimetric method was developed for this purpose and also to investigate the possible effect of adsorbent solid surfaces on the apparent dewpoint.

Measurements by the microgravimetric method

The method depends on the weight increase due to liquid condensing on to surfaces kept under controlled conditions of temperature and surrounding gas composition. The apparatus (Fig. 2) is based on a Sartorius ultramicrobalance operating with a sensitivity of 1 μg. The apparatus was designed to facilitate the passing of gas mixtures, containing known concentrations of water and sulphuric acid vapour in nitrogen, over samples held in a glass vessel suspended by a stainless-steel

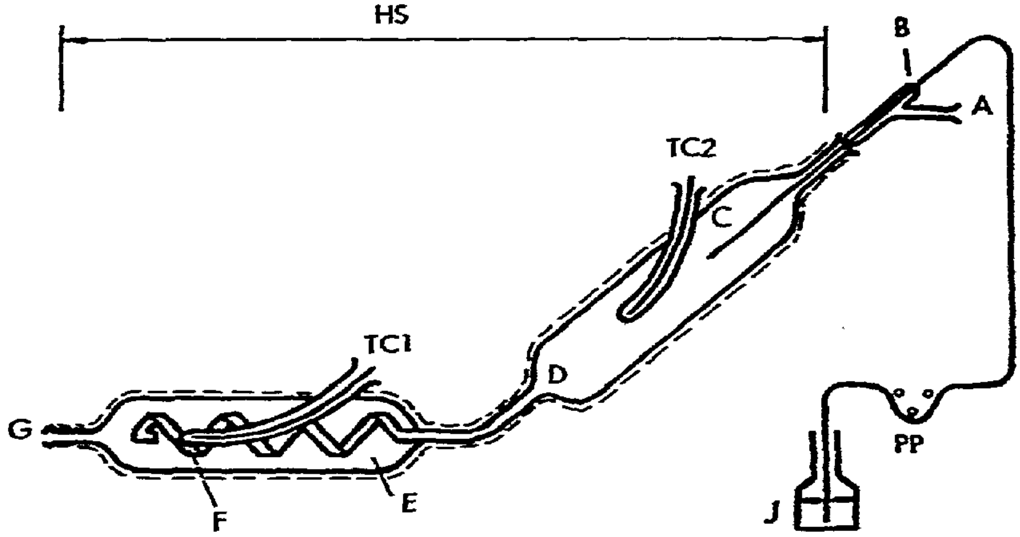

Fig. 3. Acid injection apparatus. A = gas inlet B10 socket; B = sulphuric acid solution inlet 0.5mm platinum tube; C = injection capillary 0.5mm bore; D = evaporation chamber 20mm dia 70mm long; E = expansion chamber 30mm dia 100mm long; F = mixing coil, 5 coils 3 m bore; HS = heated section; TC = thermocouples in glass pockets; G = gas outlet S13 ball joint; PP = peristaltic pump, Watson Marlow M4RE2; J = dilute acid reservoir.

wire 0.1 mm in diameter. To avoid premature condensation, it was a particular requirement of this study that the gas mixture should not be exposed to a temperature lower than that of the sample vessel at any point in the apparatus before the sample vessel. The arrangement of heaters shown in the figure was designed to achieve this condition and was based on exploratory measurements of the vertical temperature variations in the apparatus. The corrosive gases were kept away from the beam assembly of the balance by passing a proportion of the nitrogen carrier gas in through the central opening of the box surrounding the beam assembly. This has been found to be a very satisfactory and economical system for measurements in both hot and corrosive gaseous environments.

The part of the apparatus involved with injecting sulphuric acid and water into the gas stream was developed for this work and is illustrated in Figure 3. Sulphuric acid of a convenient concentration was pumped with a peristaltic pump at a rate calculated to give the desired concentrations of both sulphuric acid and water in the gas stream. The acid solution is vaporised and mixed with gas in the heated section (HS). The dewpoint measurements required a gas flow of 100 ml min^{-1} and the apparatus was designed to deliver this with sulphuric acid concentrations of 0 to 1000 vppm and water concentrations of 1 to 15 volume %. The apparatus is essentially a primary standard for sulphuric acid in a gas stream and is routinely used for calibration of analysers for sulphuric acid vapour in flue gases. The reverse process, analysis of the gas with an independently calibrated instrument, demonstrated that sulphuric acid concentrations within ± 5% of a specified value were produced by the apparatus.

The temperature of the solid sample or empty sample vessel was measured with a chromel/alumel thermocouple placed within 3 mm of the sample vessel. Calibration was effected by measuring the dewpoint of a gas mixture containing a known concentration of water vapour in the absence of sulphuric acid. This indicated that the accuracy of temperature measurement was ± 1 °C.

Acid dewpoint determinations were made with respectively (a) an empty sample vessel, (b) smut solids in the sample vessel, and (c) activated carbon in the sample vessel. The procedure was to heat initially the sample vessel to about 350 °C in flowing nitrogen, then to cool slowly in the gas stream containing the chosen concentrations of water and sulphuric acid. The temperature at which the weight recorded by the balance started to increase rapidly was noted. It was assumed, and confirmed by observations, that this increase was due to condensing acid. The increase was allowed to continue for some time (about 15 min usually) during which the temperature would fall by about another 3 °C. At this juncture, the heating was increased slightly and the temperature noted at which the weight increase ceased. Continued heating resulted in a decrease in the weight as a result of evaporating the acid which had condensed. By repeated temperature cycling the acid dewpoint could be determined to within ± 1 °C.

Experimental results and the effects of adsorbent solids

The results of measurements of acid dewpoint, over the range of gas sulphuric

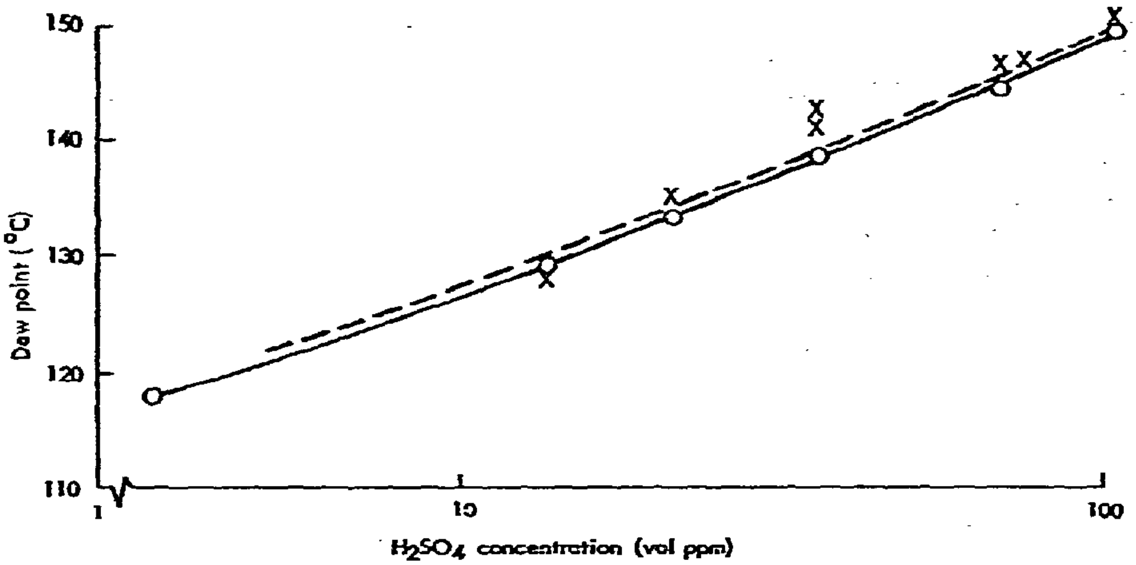

Fig. 4. Relationship between acid dewpoint and sulphuric acid concentration (water concn. 7.7 vol%). ○, Exptl points: clean system; ×, Exptl points: solids present. —, Regression line based on clean system points (○): dew point (°C) = 110.5 + 13 log $_{10}x$ + 3(log $_{10}x)^2$ x = vol ppm H_2SO_4. --, Halstead and Talbot, 1975.

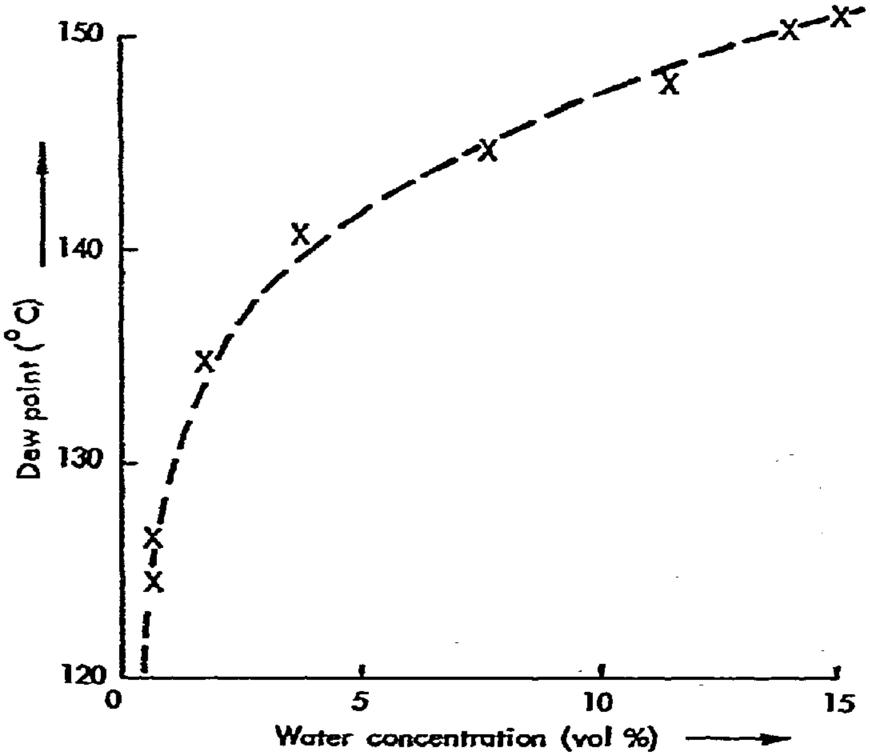

Fig. 5. Relationship between acid dew point and water concentration (H_2SO_4 concn. 75 vol ppm). ×, Exptl points; —, Regression line: Dew point (°C) = 18.7 log $_{10}V$ + 125; V = vol% H_2O.

acid concentrations 3 to 110 vppm at a water concentration of 7.7 volume %, are illustrated in Fig. 4. The experimental results correspond with the thermodynamically calculated results of Halstead and Talbot[3] to within 1 °C. The equation of the regression line for the clean system (empty sample vessel) was

$$\text{dewpoint } (^\circ\text{C}) = 110.5 + 13 \log_{10}x + 3(\log_{10}x)^2$$
$$x = \text{vppm } H_2SO_4 \tag{1}$$

95% confidence limits for this line were better than ± 1 °C. The relationship between water vapour concentration and the acid dewpoint is shown in Fig. 5. For water in the range 0.8 to 15 volume % and 75 vppm sulphuric acid, the regression equation was

$$\text{dewpoint } (^\circ\text{C}) = 18.7 \log_{10}V + 125$$
$$V = \text{volume } \% \ H_2O \tag{2}$$

The effects on the measured dewpoints of smut and activated carbon are also shown in Fig. 4. The observed differences from the clean gas data are small, + 2 °C on average, and hardly outside the limits of experimental error. Standard statistical tests on the data indicated that the measured effect was significant, the points obtained, with solid present, lying outside or at the 95% confidence limits of the line fitted for the "clean" system points.

CATALYTIC OXIDATION OF SULPHUR DIOXIDE BY CARBONACEOUS SOLIDS

It has been suggested that carbonaceous duct solids could act as catalytic adsorbents for sulphur dioxide in the presence of water and oxygen, giving rise to sulphuric acid on the surface[4]. This suggestion originated in analogy with the known phenomenon associated with activated carbons. The ultramicrobalance has been used to investigate this aspect of flue gas interactions with carbonaceous solids.

The apparatus differs from that used in the dewpoint study only in connection with the gas supply section, so that a standard test gas of 2000 vppm sulphur dioxide, 0.4 volume % oxygen, 10 volume % water and remainder nitrogen, is produced for contacting with the solid.

Study was made of activated carbon (Sutcliffe Speakman 208A) and carbonaceous duct solids obtained from an oil fired power station.

The results indicated that there was a fundamental difference in the behaviour of the activated carbon as compared with the deposit material. With the activated carbon an equilibrium weight increase of 21% was noted after more than 100 h at 150 °C and 190 °C whilst at 220 °C and 240 °C the increase corresponded with 10 ± 1 wt.%. It was necessary to raise the temperature to above 300 °C to remove all the adsorbate. This, with combined weight and sulphur determinations, indicated that sulphuric acid was indeed formed on the activated carbon surface with a maximum equilibrium content of 21 wt.%. With the power station deposit material, adsorption was much less. At 110 °C the measured weight increase due to adsorption was only 0.5 wt.%, whilst at temperatures higher than 110 °C no adsorption was detected.

It has been observed by earlier workers that some oil cokes adsorb sulphuric acid at temperatures higher than the acid dewpoint[5]. Additionally, analyses of flue gas solids sampled above the acid dewpoint have indicated acid contents of 1 to 4 wt.%. No systematic detailed study had been reported and the ultramicrobalance was obviously suitable for this. Adsorption of sulphuric acid was determined on a smut sample collected at an oil fired power station and studied in some detail previously[6] and on activated carbon (Sutcliffe Speakman 208A).

The apparatus was that used in the dewpoint study (Fig. 2) but the procedure was different, though not unusual. The initial phase of all the adsorption measurements was heating of the sample to 350°C in flowing nitrogen. When constant weight had been achieved, indicating complete removal of condensed and adsorbed water and sulphuric acid, the sample was allowed to cool in flowing nitrogen to the temperature at which adsorption was to be determined. After the attainment of the desired steady temperature the gas composition was altered to give the required sulphuric acid and water concentrations. The increase in weight to a new constant value was measured. Variables investigated for the smut were sulphuric acid concentration, water concentration and temperature. Figures 6 and 7 show, respectively, the relationship between adsorption capacity and temperature for one gas composition (38 vppm sulphuric acid, 7 volume % water and 93 volume % nitrogen) and the adsorptive capacity as a function of sulphuric acid concentration at one temperature (the 170°C "isotherm").

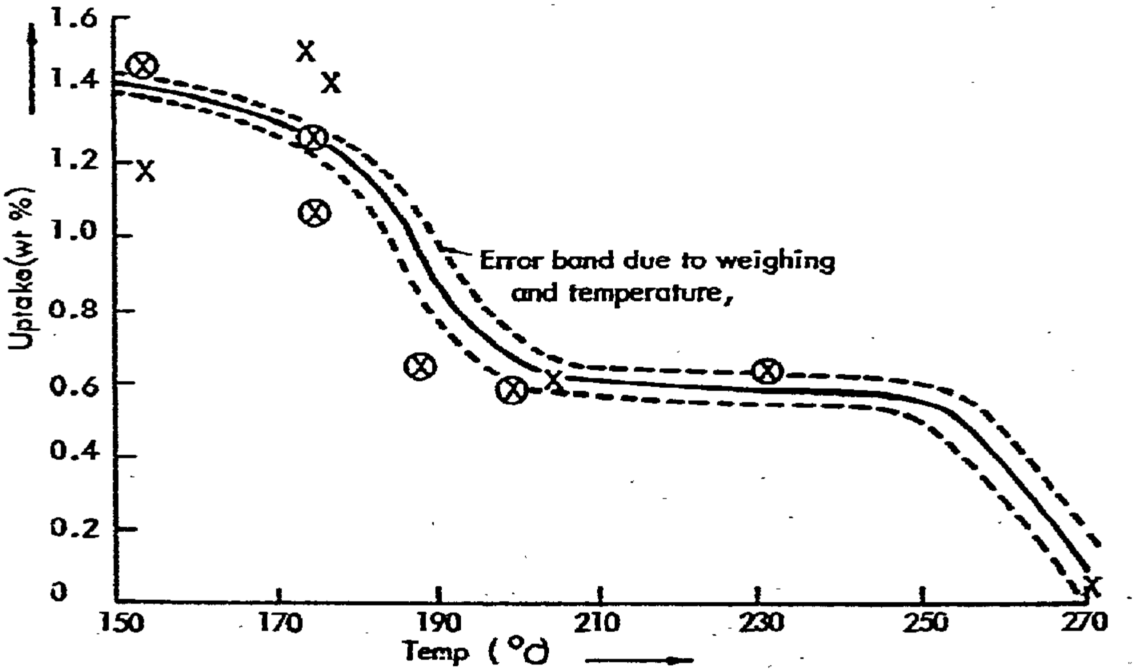

Fig. 6. Sulphuric acid adsorption on smut at different temperatures (gas composition 38 vppm H_2SO_4 8 vol % H_2O). ×, Sample 1; ⊗, sample 2.

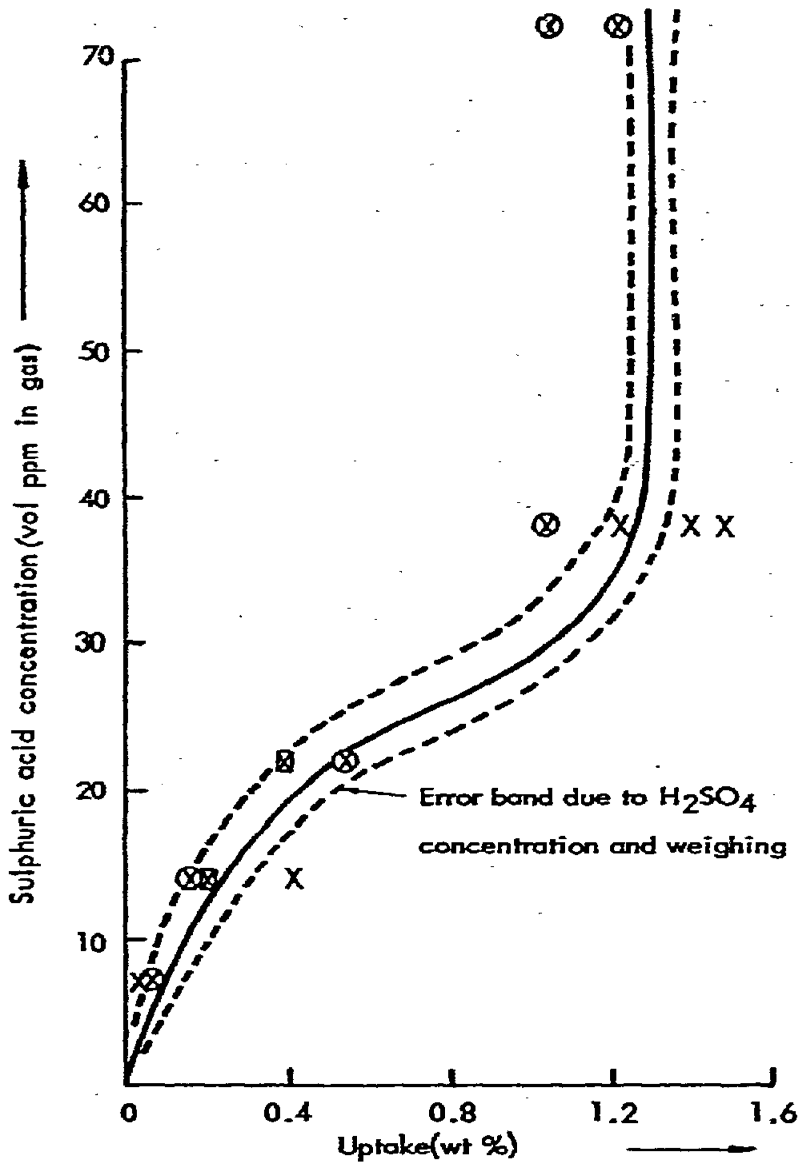

Fig. 7. The 170°C isotherm for sulphuric acid adsorption on smut. ×, Sample 1; ⊠, sample 2; ⊗, sample 3.

For comparison with the smut, the adsorption of sulphuric acid on activated carbon was also determined. The rate was very slow (200 to 300 h to equilibrium) so that it was possible to make duplicate measurements at one condition only; 38 vppm sulphuric acid, 7 volume % water and 93 volume % nitrogen at 170 °C. The equilibrium uptake was 31 wt.%. We ascribe the slower rate of adsorption in the case of the activated carbon to the highly microporous nature of this adsorbent. Almost the whole of the active surface of a poor adsorbent like smut is accessible with little necessity for internal diffusion, whilst in the case of high capacity adsorbents, such as the commercial activated carbons, access to most of the active surface involves diffusion down long micropores.

The saturated equilibrium adsorption capacities on the smut in the temperature range 150 to 180°C (10 to 40°C above the acid dewpoint) and on the activated carbon at 170°C both correlated with the values calculated assuming monomolecular coverage of the adsorbent surface. Thus, the surface area occupied by a sulphuric acid molecule on an adsorbent surface (σ_{ms}) can be calculated from the expression[7]

$$\sigma_{ms} = 3.464 \times 10^{16} (M/4\sqrt{2}\, N_A\, \delta_L)^{2/3} \qquad (3)$$

Here M is the molecular weight of the adsorbate, N_A is Avogadro's number and δ_L is the density of the adsorbate in the liquid phase.

Equation (3) results in $\sigma_{ms} = 0.44$ nm^2 for sulphuric acid. Taking the surface area of the smut as 25 m^2 g^{-1} (a typical value for power station duct deposits as measured by xenon adsorption at 0°C; Street, 1975, private communication), the calculated adsorption capacity is 0.93 wt.%. Considering the approximations involved in the calculations this is in reasonable agreement with the experimental value of 1.1 to 1.5 wt.%. For the activated carbon, the calculated equilibrium adsorption was 37 wt.% (on the basis of a surface area for this material of 1000 m^2 g^{-1}, determined by krypton adsorption, Jameson, 1974, private communication). This shows good agreement with the experimental value of 31 wt.%.

The form of the isotherm for the smut at 170°C also indicates that the process occurring is monomolecular layer adsorption on the homoenergetic surface. This is unlikely to represent the process in detail but, rather a satisfactory approximation. Experiments with different concentrations of water in the gas phase showed that there was no detectable difference for water concentrations from 1.6 volume % to 12.3 volume %.

CONCLUSIONS

An apparatus has been developed incorporating a simple and effective modification to the gas flow system of a Sartorius ultramicrobalance which eliminates contact between the balance mechanism and corrosive gases. This has been used to provide "mechanistic" information relevant to acid smut formation by investigating interactions between sulphuric acid in the gas phase and carbonaceous solids.

These studies lead to the following specific conclusions with reference to power station operation and the avoidance of acid smut formation and emission.

(a) The thermodynamically predicted acid dewpoint–sulphuric acid gas phase concentration relationship for "clean" gases has been confirmed.

(b) The catalytic oxidation of sulphur dioxide on duct deposits makes a negligible contribution to acid smut formation.

(c) The adsorbed acid content of carbonaceous duct deposits (1 to 2 wt.% at temperatures up to 40°C above the acid dewpoint) will not play a significant role in acid smut formation, particularly as it is not in the form of an adhesive liquid film.

This level of acid is important when duct deposits are considered more generally in that it provides a mechanism of acid transport above the dewpoint. Thus, although the precaution of maintaining plant surfaces above the acid dewpoint precludes the formation of acid smuts (see conclusion a) it does not ensure that surface deposits will be free of acid.

ACKNOWLEDGEMENTS

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