

Adsorption of Ammonia on Coal Fly Ash

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ABSTRACT

The adsorption of ammonia on coal fly ash is of concern whenever SCR or SNCR technology is utilized for mitigation of NO_x emissions from coal fired boilers. The problem is associated with “ammonia slip” in which some portion of the ammonia intended for NO_x reduction escapes into the flue gas, and in this case, adsorbs onto the coal fly ash. This ammonia content renders the fly ash less marketable, as the ammonia tends to be released when the ash is used as a pozzolan in concrete. Because of the commercial interest in this issue, a fundamental study of ammonia adsorption on fly ash was undertaken. This study has shown that at high ammonia concentrations, the unburned carbon in the fly ash serves as the main site for ambient temperature adsorption. The amounts of uptake are predictable from standard BET-type measurements. On the other hand, the amounts of uptake seen in pure ammonia adsorption experiments are far less than what is observed in the field. This indicates that either (or both) the elevated temperatures in actual flue conditions, or cooperative effects involving other flue gas components, play an important role in enhancing the reversible uptake of ammonia.

INTRODUCTION

There has been a large impetus given to development of post-combustion NO_x control strategies by the Clean Air Act Amendments and by the impending new ozone regulations. The leading candidates for meeting the challenges are selective non-catalytic reduction (SNCR) and the closely related selective catalytic reduction (SCR). In these processes, ammonia or related compounds are injected into the flue gas, to help reduce NO. If not properly controlled, there is a chance of excess ammonia escaping together with the flue gases, giving rise to the so-called “ammonia slip” phenomenon. Ammonia can actually exit with the stack gases or, as is of main interest here, it can be adsorbed onto the surfaces of fly ash. The presence of ammonia on fly ash represents a serious problem, as regards utilization of the ash. There have already been numerous reports of ammoniated fly ash being deemed unacceptable for construction uses, because of the release of ammonia that occurs when the fly ash is wet with water (such as when the fly ash is used as a pozzolan). It is therefore necessary to characterize the nature of the interaction of ammonia with fly ash, to help in the search for a solution to this problem.

There have been few studies of the problem to date. In one study¹, the adsorption of ammonia from simulated flue gases was examined on both coal and oil fly ashes. The temperature range of interest was approximately 120-160°C (393–433 K) and the ammonia concentration

ranged from 0 to 20 ppm. These values were selected as representative of a boiler air heater outlet. Based upon those results, several hundred to several thousand ppm levels of ammonia were measured in the ashes so treated. Field reports of several hundred ppm ammonia in ash are not uncommon¹. There appeared to be no correlation of ammonia uptake with loss on ignition (LOI, or carbon content), with BET surface area of the ash or with pH levels in the ash. Coal ashes generally showed a decrease in uptake with increase in temperature, but the temperature dependence was not strong. Uptakes were typically in the range from 200-600 ppm by mass.

Another study² has shown that the temperature dependence of ammonia uptake on coal ash is considerable, when observed over the temperature range from 0 to 500 °C. The uptake was observed to decrease to a minimum at about 350°C. The uptake at near ambient temperature was around 600 ppm by weight for a gas phase ammonia concentration of 500 ppm. Pretreatment of the ash at temperatures of 200 °C and 350°C caused the sorption capacity of the ash to drop measurably. It was calculated that the uptake of ammonia on the pretreated ashes approached near-monolayer capacity, relative to BET surface areas. It was concluded from this work that physisorbed water plays an important role in ammonia uptake below 120°C on untreated ashes; the ammonia is believed to be absorbed by the water. There was only a weak dependence of ammonia adsorption capacity with ammonia concentration above about 50 ppm, up to almost 800 ppm².

It may be concluded when examining the above studies that there is yet a great deal to be understood about the ammonia adsorption process on fly ash. The complications inherent in having both an inorganic ash phase and carbon in the same system are partly to blame. The problem of ammonia adsorption on carbon is itself complicated. There have been a significant number of studies concerned with the adsorption of ammonia on carbons. Most of these studies have been performed at concentrations higher than those of interest in connection with the ammonia slip problem.

It is important to distinguish between the different ways in which the ammonia is adsorbed on carbon surfaces. One clearly established feature is that oxide groups on the surface of a carbon enhance the adsorption of ammonia onto the surface. It is often hypothesized that the acidic functional groups associated with the surface oxides act as Bronstead acids towards ammonia, which is a strong base³. These acid functionalities donate a proton to the ammonia in an acid-base interaction, yielding an ammonium ion, NH_4^+ . The suggestion has been made that the ammonia reacts with surface acid groups⁴, probably yielding amides, or possibly even imides^{3,5}. As the temperature of the complexes is raised, the irreversibly formed amide groups can decompose, eventually giving rise to cyano groups on the carbon surface⁴. Hence, the adsorption process involving reaction of ammonia with acid groups to form amides would be observed as irreversible, even to high temperatures.

Heat treatment of a carbon prior to adsorption changes the ammonia isotherms from a Type I to Type III⁶. The latter isotherm indicates a weak gas-solid interaction. Heat treatment would generally involve loss of oxygen functionality from the surface. The effect of addition of oxides has also been studied. It has been clearly demonstrated that increased oxidation of a surface enhances the uptake of ammonia by the carbon surface⁷. It has earlier been suggested

that the polarity of the fly ash carbon surface has a profound effect on the ability of the fly ash to adsorb air entraining agent (AEA)⁸⁻¹⁰. In the case of an AEA, which is fundamentally a non-polar molecule with a polar endgroup, the adsorption of AEA is decreased with increased surface oxidation or polarity. Oxygen functional groups impart polarity to the surface. Thus, the adsorption of ammonia and AEA follow opposite trends, with regard to oxidation of the surface.

The heats of adsorption on such carbons are typically around 6 to 6.5 kcal/mol^{5,11}. These values are close to the heat of condensation of liquid ammonia (near 5.2 kcal/mol at 273 K⁶ and 6.1 kcal/mol for the subcooled liquid at 195 K¹²) and the heat of sublimation of solid ammonia (7.4 kcal/mol)⁶. By way of contrast, the heats of ammonia adsorption on carboxyl groups have been characterized to involve values of between 21 and 15 kcal/mol⁴.

It should also be noted that the critical temperature of ammonia is 405.5K. Thus some of the earlier cited studies on fly ash involved temperatures in excess of the critical temperature of ammonia. Generally speaking, the adsorption capacities of solids for gases above their critical temperatures are quite low, when ordinary ambient pressures are involved.

Motivated by the increasing importance of understanding the problem of ammonia adsorption on fly ash, a study of pure ammonia adsorption was undertaken. It was recognized at the outset that these tests would not necessarily simulate the conditions seen in actual flue gas. On the other hand, it was felt useful to understand better how much of the observed field behavior could be explained by simple adsorption phenomena, and how much had to do with the particular situation that exists in a coal boiler.

EXPERIMENTAL

The surface area and porosity of fly ash samples were characterized using standard volumetric gas adsorption experiments. These experiments were performed using an Autosorb-1 system from Quantachrome Corp. The fly ash samples were placed into the appropriately sized sample holders and were outgassed for several hours at constant temperature (573 K) in vacuum prior to analysis.

In adsorption experiments involving N₂ as the adsorbate, the customary temperature of 77 K was maintained using a liquid nitrogen bath. In the adsorption experiments involving CO₂ and NH₃, a bath temperature of 273 K was maintained using ice and water. At a temperature of 273 K, the generally accepted¹³ saturation pressure for liquid CO₂ is 26144.1 torr (= 3484.8 kPa). There remains some controversy in the literature regarding the phase of the sorbed CO₂, especially as regards the density of the sorbed layer. This reflects itself in an enormous range of values being reported for its sorption cross-section¹⁴. Meanwhile, the very high value of saturation pressure, taken together with the operating limits of the available device (760 torr maximum pressure) suggests that CO₂ will only be useful for exploring microporosity. The experiments were, however, conducted below the critical temperature for CO₂, which is 304.14 K.

The saturation pressure for ammonia at 273.15 K is 429.62 kPa (=3223 torr)¹⁵. Again, the critical temperature for ammonia is 405.5 K, so these experiments were conducted well below the critical point for this gas.

The Brunauer, Emmet and Teller (BET) theory¹⁶ was used for calculating surface areas and Dubinin-Radushkevich (DR) theory¹⁶ has been used for determining the microporosity of the fly ash samples. It should be recalled that the earlier reported work⁸ established that the main source of micropores in fly ashes is unburned carbon.

As is standard in the literature, the convention used here involves calling any pores smaller than 20 Å in width “micropores”, any pores between 20 and 500 Å “mesopores” and pores larger than 500 Å “macropores”.

RESULTS

The comparative study of the adsorption behavior of different gases on fly ash was carried out using a representative class F fly ash sample from our sample bank (Fly Ash 21, according to our designation)⁸. This sample is typical of a class F ashes produced in pulverized firing, and has an LOI of 6.1%. The sample was provided by the Brayton Point Power Station in Fall River, Massachusetts. This fly ash sample had been previously analyzed using standard foam index techniques, and shows itself to be very active towards AEA adsorption⁸.

Preliminary Characterization of Sample Porosity

The nitrogen adsorption isotherm for this sample is shown in typical form in Figure 1. The ordinate is STP cc of gas adsorbed per gram of solid and the abscissa is relative pressure of the adsorptive (in this case N₂) P/P₀, where P₀ is the saturation vapor pressure of N₂ at the temperature of the experiment (760 torr for the liquid nitrogen used here).

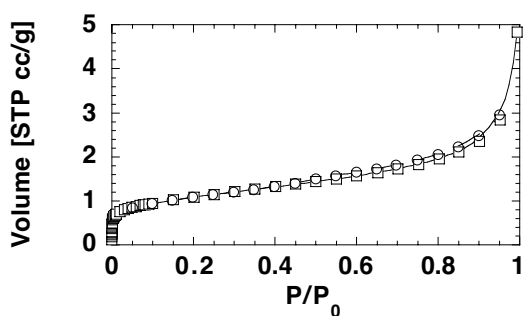


Figure 1. Nitrogen isotherm (77 K) for fly ash 21.

This type of isotherm is characteristic of microporous samples. The fact that the isotherm is seen to rise very steeply at very low relative pressure is indicative of sample microporosity. A very good linear BET plot is obtained, and a nominal surface area for the whole fly ash is 3.7 m²/g. Earlier we reported on similarly obtained nitrogen isotherms on this and other ashes⁸. From the earlier data obtained on the mineral part alone, after complete carbon removal by combustion, it was possible to back-calculate the surface area contribution from the carbon alone.

The value that was obtained, 49 m²/g-carbon, is very typical of the values seen for a great number of carbons from class F ashes.

The DR plot for the isotherm results of Figure 1 is shown in Figure 2. This plot is seen to be very linear in the micropore region, and it appears that a good estimate of micropore volume is therefore available. The DR plot provides a micropore volume estimate of $1.5 \cdot 10^{-3}$ cc/g, which is attributable almost entirely to the carbon in the ash.

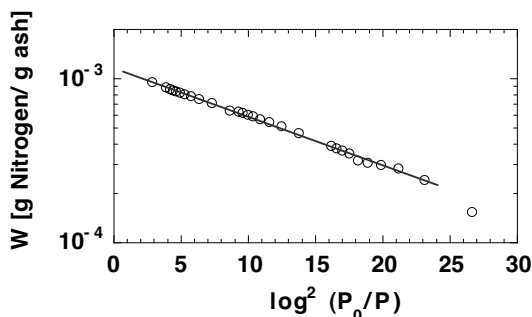


Figure 2. Dubinin-Radushkevich plot for N₂ on fly ash 21

Use of CO₂ adsorption isotherm data (presented below) in a DR-type of analysis suggests that the estimate obtained from nitrogen might have included some supermicropores and mesopores. This topic will not be addressed in detail here, because generally speaking, the CO₂ values supported the micropore volume estimates obtained using nitrogen. The implication of the above results is that the carbon in this class F fly ash contains a significant amount of microporosity, probably characterized by a wide distribution of sizes. The inorganic fraction of the ash contains very little microporosity, and contributes little to the low pressure portion of the isotherm.

Ammonia Adsorption

Ammonia is not a common choice of adsorptive for studying porous materials. It is a polar molecule, which means that it would be expected to have a significant polarity mismatch with normally non-polar carbon surfaces. It was therefore anticipated that the isotherms of ammonia on fly ash would show relatively low uptake. Three replicate experiments were performed with ammonia on fly ash sample 21. All gave quite reproducible results. A typical isotherm is shown in Figure 3. Note that because the saturation pressure of ammonia at 273 K exceeds 760 torr, the experiments were only performed up to a relative pressure of approximately 0.25.

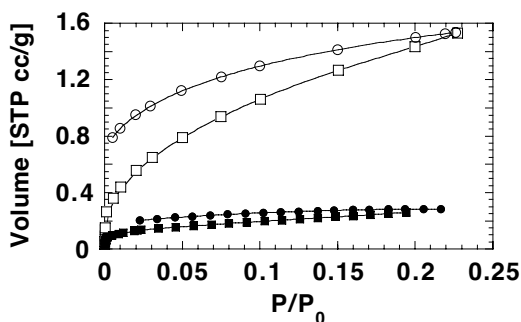


Figure 3. Ammonia isotherms on fly ash 21. Open points - whole fly ash, closed points- fly ash with carbon removed. Squares- adsorption, circles - desorption

The ammonia isotherms showed a significant degree of hysteresis, as is evident from Figure 3. In addition to the hysteresis, it was noted that desorption times became extremely long, during the low pressure desorption experiments. These results are suggestive of an irreversible sorption process. This would not be surprising, given that the earlier cited literature suggested this as a possible result of reactions with functional groups on the carbon.

The ammonia isotherms permitted calculation of a BET surface area; the value obtained was approximately 5.4 m²/g. This value is a bit higher than the surface area calculated from the nitrogen results, but there were a significant number of assumptions that went into the calculation. First, the coverage area of the ammonia molecule had to be estimated from liquid ammonia densities. The value which was obtained and used in the subsequent calculations was 14.0 Å². Also, despite the knowledge that the isotherm showed evidence of hysteresis, probably due to irreversible reaction, it was assumed that the simple BET physisorption model applied to the adsorption results. In view of these issues, the surface area obtained here was in surprisingly good agreement with the nitrogen BET value. Use of the desorption branches of the isotherms gave an area of 4.7 m²/g, in even better agreement with the nitrogen values.

The information of most interest with respect to the ammonia slip issue is contained in the region of the isotherm most near the zero relative pressure axis. To show the behavior at low pressures more clearly, the isotherms can be plotted on a logarithmic scale. The results are shown in Figure 4. A very notable feature of Figure 4 is the sudden increase in adsorption volume near a relative pressure of 10⁻⁴. This feature was reproducible in all of the experiments with the as-received fly ash 21 sample. A similar feature is not visible, at either the same relative pressure or at the same absolute pressure, in the results from nitrogen and carbon dioxide. A comparison of the isotherms for all three of these adsorptives is shown in Figure 5.

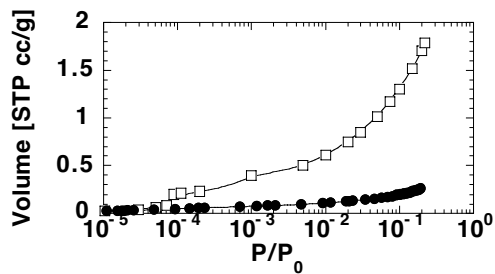


Figure 4. Ammonia adsorption isotherms of Figure 6 shown on logarithmic relative pressure scale.

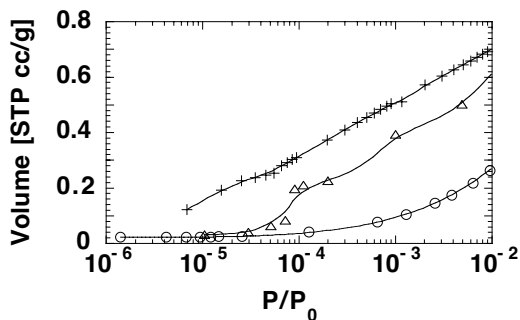


Figure 5. Comparison of N₂ (crosses), NH₃ (triangles) and CO₂ (circles) isotherms.

In the very low relative pressure range associated with filling the smallest micropores, ammonia, carbon dioxide and nitrogen all show somewhat comparable behavior and adsorption amounts. There are, of course, significant differences as well. The ammonia shows the already described abrupt change in slope of the isotherm. The absolute amounts of adsorption differ by a factor of three or more, for the three gases.

Ammonia shows behavior intermediate between that for carbon dioxide and that for nitrogen. Still, it is fair to conclude that the physical adsorption process governing ammonia adsorption at near ambient conditions is quite similar to that seen with both nitrogen and carbon dioxide, at comparable relative pressures.

The adsorption behavior of ammonia on this fly ash sample is dominated by the adsorption on carbon in the fly ash. This is consistent with an earlier similar conclusion regarding the

relative roles of carbon and mineral components in nitrogen adsorption. The relative contributions of the two components may be judged from Figure 4, which shows a comparison of the whole ash isotherm (already discussed) with the isotherm for the ash with the carbon completely removed. It is clear that most of the adsorption takes place on the carbon. Bearing in mind that the carbon represents about 6 % by mass of the whole ash, the importance of the carbon in the adsorption process is put into very clear perspective.

The ammonia-BET surface area of the carbon-free ash is $0.7 \text{ m}^2/\text{g}$, which is in excellent agreement with the values earlier obtained from nitrogen isotherms. The fact that there is good agreement between nitrogen and ammonia BET values for the carbon-free ash is not necessarily inconsistent with the less good agreement between these values for the carbon-containing ash. This is because most of the surface area in the mineral portion of the ash is external surface area. For illustration, a spherical particle of $10 \mu\text{m}$ diameter and 1 g/cc density would have an external surface area of $0.6 \text{ m}^2/\text{g}$, in reasonable order of magnitude agreement with the above estimate.

The comparison in Figure 4 emphasizes the low relative pressure results. The contribution of the mineral portion is seen to be very small in comparison with the contributions of the carbon, particularly after the sudden jump at a relative pressure of about 10^{-4} . A relative pressure of 10^{-4} represents an absolute pressure of 0.32 torr. In a gas mixture at atmospheric pressure, this ammonia partial pressure would represent a concentration of roughly 420 ppm. In the range of 20 ppm, as might be involved in the ammonia slip problem, the corresponding relative pressure would be below 10^{-5} .

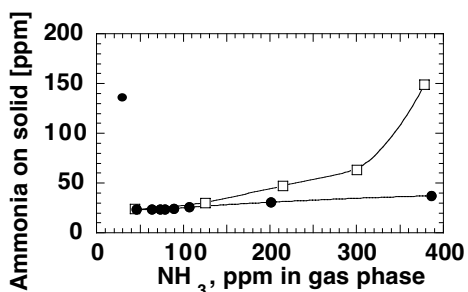


Figure 6. Low relative pressure end of the ammonia isotherms. Open points- whole ash, closed points- carbon free ash. Circle shows lowest Muzio et al. value.

The few results that are available in the neighborhood of 10^{-5} relative pressure at 273 K are shown in Figure 6. The results have now been replotted to show them in terms of units that are commonly encountered in the field, ppm by weight of ammonia in the solid as a function of ppm of ammonia in the gas phase. These results still show that the carbon-containing sample exhibits a greater uptake than the carbon-free sample, but the differences get small at the low end of the relative pressure range. It appears that under low concentration (ammonia slip) conditions, it is the mineral component of the ash that dominates the behavior.

It would be dangerous to infer from these results that the mineral will necessarily dominate the behavior under field conditions. For one thing, the uptake in these pure ammonia adsorption experiments is far lower than those obtained by Muzio et. al¹ in their experiments (see Figure 6) or in typical field results. The reason for the discrepancy between the values observed in the field and the present isotherm is not yet understood. It might be that the present sample has an unusually low capacity. We do not believe this to be the case, though, insofar as Muzio's samples all gave much higher capacity, and his sample set included quite

similar samples. On the other hand, the influence of processing conditions also cannot be overlooked. It is possible that SCR and SNCR processes somehow create greater ammonia capacity in ashes that is not duplicated during laboratory testing of a non-SCR ash. This could possibly involve a change in the carbon surface oxide population, or a creation of a sorbed water layer on the carbon. We do not, however, have any evidence from the many ashes in our sample bank that such a difference exists. A third possibility may be inferred from the literature on carbon blacks. There has been reported a very slight increase in ammonia adsorption capacity with temperature in carbon blacks^{6, 12}. This is contrary to the temperature trends observed in the earlier work on ashes, however.

It must also be recalled that the present results are entirely consistent with the observations by Turner² that ammonia on outgassed (“pretreated”) fly ash is held to an extent which is comparable to that revealed by ordinary surface area probing techniques. Our samples were outgassed at 300°C, so they should be comparable to his “pretreated” samples. Moreover, Turner’s experiments were performed in dry flowing gas, so the adsorption conditions were also quite comparable to ours. This dry ammonia adsorption process explained about 2/3 of the capacity of the as-received ash for ammonia in Turner’s work. The remaining capacity was hypothesized by Turner to be due to moisture and oxides on the ash surfaces, which are lost on heating. We believe that our work has made it clear that it is the carbon in the ash that is mainly responsible for this dry adsorption capacity. Thus in seeking an explanation of the difference of our results from the Muzio et al. results, it should be kept in mind that the pure ammonia adsorption results seem to have independent confirmation.

The experiments of Muzio et al. differed from ours in one important respect. Their experiments were conducted with the ammonia in humidified and acid-gas (SO₂) containing air. The absorption of ammonia by water or acid sites could well have played some role in yielding the high capacities that they observed. In the absence of the acid component in the gas, the ash itself would have very little moisture content at the temperature of their experiments. Data are available on solutions of ammonia and SO₂ in water¹⁷. The partial pressures of ammonia and SO₂ above such solutions are given by:

$$p_{\text{NH}_3}(\text{torr}) = F_2(T) \frac{C(C-S)}{(2S-C)^2}$$

$$p_{\text{SO}_2}(\text{torr}) = F_1(T) \frac{(2S-C)^2}{C-S}$$

where

$$\log_{10} F_1(T) = 5.865 - [2368 / T(\text{K})]$$

$$\log_{10} F_2(T) = 13.680 - [4987 / T(\text{K})]$$

The parameter C represents the concentration of NH₃, in mols/100 mols of water, and the parameter S the concentration of SO₂ in mols/100 mols of water. The actual correlations were developed for the temperature range from 308 K < T < 363 K, and ammonia concentrations in the range 5.8 < C < 22.4 mols/100 mols water. Clearly these correlations are intended for conditions somewhat outside of the current range of interest, but it is instructive to examine the implications of an extrapolation.

A short temperature extrapolation is possible to the lower end of the temperature range examined by Muzio et al. ($T = 120\text{ }^{\circ}\text{C} = 393\text{ K}$). At this condition, $F_1 = 0.691$ and $F_2 = 9.78$. It may be shown that:

$$P_{\text{NH}_3}P_{\text{SO}_2} = F_1F_2(2y+C)C$$

and that

$$P_{\text{NH}_3} = F_2 C y / (-2y + C)$$

where $y = (C - S)$. It can also be shown that the solutions to this pair of equations will normally yield values of $y \ll C$, for the conditions of present interest. In this case,

$$P_{\text{NH}_3} \approx F_2 y$$

and

$$P_{\text{NH}_3}P_{\text{SO}_2} \approx F_1F_2C^2$$

For $P_{\text{NH}_3} = 20\text{ ppm} = 20 \cdot 10^{-6} \cdot 760 = 1.52 \cdot 10^{-2}\text{ torr}$ and $P_{\text{SO}_2} = 1500\text{ ppm} = 1500 \cdot 10^{-6} \cdot 760 = 1.14\text{ torr}$, $y = 1.55 \cdot 10^{-3}$, $C = 0.051$ and $S = 0.049$. These values are excellent approximations to the actual exact solutions. To the extent that the extrapolations involved reflect the real situation in an ash particle, it is possible to estimate the moisture content on the particle surface. If f represents the fraction by mass ammonia on the particle, then this quantity must be given by:

$$f = C \cdot m \cdot (100\text{ mol. water} / 1800\text{ g-water}) \cdot 17\text{ g NH}_3/\text{mol NH}_3$$

where m is the g-moisture/g-ash. Assuming a typical f value of 200 ppm, the moisture content in this case would be 0.4%, assuming that all of the ammonia is held in the water phase.

The above calculation illustrates only that a small water film, assuming that it exists and that it can be modeled using bulk phase behavior, can explain a significant enhancement of ammonia capacity. At 120°C , the vapor pressure of water above an SO_2 solution with $S = 0.49$ would be around 1480 torr, in the absence of the ammonia¹⁷. This is sufficiently high that it is not clear that a water film is even possible under the conditions used by Muzio et al. Still, it appears that the most plausible explanation for the considerably higher ammonia capacity observed in that study compared with ours is that there is some interaction of ammonia with SO_2 in the condensed phase.

The above discussion is only intended to point out the importance of studies on co-operative adsorption in these systems. There are many facets of these processes that it would be difficult to reliably predict without actual measurements. These calculations also serve to highlight the care that needs to go into any experimental study of this kind. A slight decline in temperature, which might promote some condensation of moisture, can enormously impact the apparent capacity of an ash for ammonia.

CONCLUSIONS

The present study has shown that pure gaseous ammonia may be reversibly adsorbed onto the surfaces of fly ash under ordinary ambient conditions. The amount of adsorption is predictable from the surface area of the ash, and unburned carbon can play a dominant role in providing such surface. The present results also confirm that there is some extent of irreversible chemisorption, presumably associated with the oxides on the carbon surface. The extent of

reversible physical adsorption of ammonia onto the carbon surface is quite comparable to that taking place in nitrogen or carbon dioxide, under comparable relative pressure conditions.

The present results do not, however, model the much larger uptakes of ammonia reported in field samples. It is tentatively concluded that these higher uptakes must be associated with more complex chemistry involved in actual multicomponent flue gas mixtures, and/or with the slightly higher temperatures involved under the field conditions. These higher temperatures are quite near or above the critical point for ammonia, meaning that the simple physical adsorption processes studied here could not occur until the samples cooled down. On the other hand, the higher temperatures can certainly promote chemisorption reactions. These possibilities are being explored.

ACKNOWLEDGMENT

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