FORMS OF AMMONIA ON SCR, SNCR, AND FGC COMBUSTION ASHES

Aurora M Rubel

University of Kentucky
Center for Applied Energy Research
2540 Research Park Drive
Lexington, KY 40511

Introduction

An understanding of the forms of ammonia captured by combustion fly ash in response to selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), and flue gas conditioning (FGC) for ESP particulate separation conditions has been the focus of work at the Center for Applied Energy Research. The thermal release properties of ammonia from 8 ashes produced at power plants using SCR, SNCR, and FGC conditions were found to have widely different onset and peak evolution temperatures suggesting different forms of captured ammonia[1]. A study of two ashes, one produced under SCR and the other under SNCR conditions confirmed significantly different onset and peak thermal release temperatures as well as major differences in the associations between ammonia, sulfate, and residual carbon and ammonia thermal release rates[2]. Further work to understand the influence of SCR and SNCR in determining the form of ammonia captured by combustion ashes indicated that ammonia was primarily associated with sulfate in both SCR and SNCR ashes. The ammonia in SCR ash was less stable showing changes in its association with sulfate and thermal release properties with the length of time from combustion; whereas, ammonia in SNCR ash remained relatively unchanged [3].

The focus of the current work was to identify the specific form of ammonia in SCR, SNCR, and FGC ashes and to investigate the influence of the ash matrix on the thermal release of the captured ammonia. Comparisons were made between ammonia released from ash, ammonium salts and salts blended with model matrices.

Experimental

Materials. Three ashes were used from utilities employing either SCR, SNCR, or FGC. The ashes were kept in airtight containers from collection and throughout the study. Materials used as model substrates were alumina and ash heated to 900°C in a muffle furnace. Recently purchased 99.9% pure ammonium hydrogen sulfate (AHS) and ammonium sulfate (AS) were used alone and blended to 500 ppm NH_3 with the model substrates.

Analytical Methods. The ash samples were subjected to ammonia determinations by an ion selective electrode method[4]. Elemental analysis for C, H, N, S and loss on ignition (LOI) determinations were done by standard procedures.

The thermal properties of ammonia release from the ashes, pure salts, and the blends were determined by thermal analysis – mass spectrometry (TG-MS) using a Netzsch Jupiter STA 449C thermal analyzer coupled to a Balzer Thermostar QMS. The sample size was 500 mg for the ashes and salt blends and 2 mg for the pure salts. Other TG conditions have been previously described[1-3]. Each sample was run in triplicate to confirm reproducibility.

Mass spectra were acquired every 10 seconds in multiple ion detection (MID) mode. Identification of ammonia was done by calculating the ratio of the MS signals for mass 17 (primary mass for ammonia) divided by mass 18 (primary mass for water).

Results and Discussion

The chemical characterization of the combustion ashes is shown in Table 1.

Table 1. Chemical Characterization of Study Ashes

	SCR	SNCR	FGC
ppm NH_3	680	330	245
%C	0.9	32.2	6.9
%H	0.08	0.07	0.04
%N	0.01	0.5	0.06
%S	0.9	0.3	0.2
LOI	4.8	28.6	8.1

The ammonia evolution profiles from the SCR, SNCR, and FGC ashes are shown in Figure 1. Different ammonia release patterns were found consistent with previous results from our laboratory[1-3]. Onset temperatures for ammonia evolution form the three ashes were 200, 260, and 300°C for SCR, FGC, and SNCR ashes respectively. In all cases, SO_2, a decomposition product of sulfate, was determined by MS to be the primary gas released from the ash which was associated with ammonia.

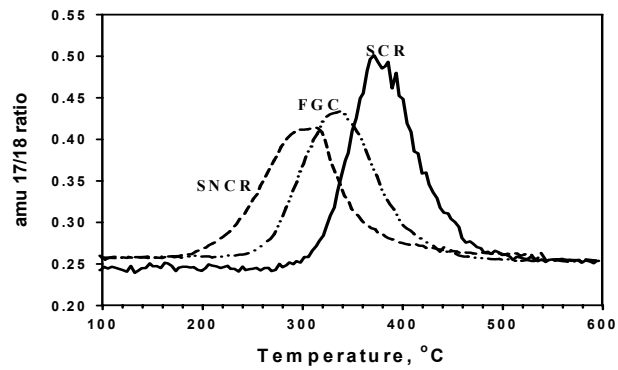

Figure 1. Ammonia evolution from SNCR, FGC, and SCR ashes.

Previous work suggested the two likely candidates for the ammonia storage vehicle in combustion ash is AHS or AS[1-3]. Therefore, these two ammonium salts and their mixtures in model matrices, alumina and ammonia-free ash, were subject to the same heating regimes as the ashes (Figure 2 and 3). The concentration of the ammonia in the blends was 500 ppm so as to be in the same concentration range as the ashes. In order to avoid problems associated with overwhelming the MS detectors and from the condensation of SO_2 in the heated capillary transfer line from the TG furnace to the MS, only 2 mg of the pure salts were heated. Both these factors can affect the detected ammonia release properties. These issues and the integrity of samples of AS and AHS used in a previous study[1], raised concern about the validity of our earlier results for the ammonia release temperatures for these salts. Newly acquired chemicals were, therefore, used in this study. AHS alone decomposed at a higher temperature than AS. Ammonia release started at 390°C vs 210°C for AS. This was a reversal of previous results which indicated a lower decomposition temperature for AHS and justified our concerns with the ammonium salts previously used in our laboratory. Presently, a number of ammonium sulfates from different sources are being compared.

Decomposition of AHS only occurred in one step both with respect to weight loss and detection of ammonia by the MS. However, blending with either alumina or ash markedly changed the

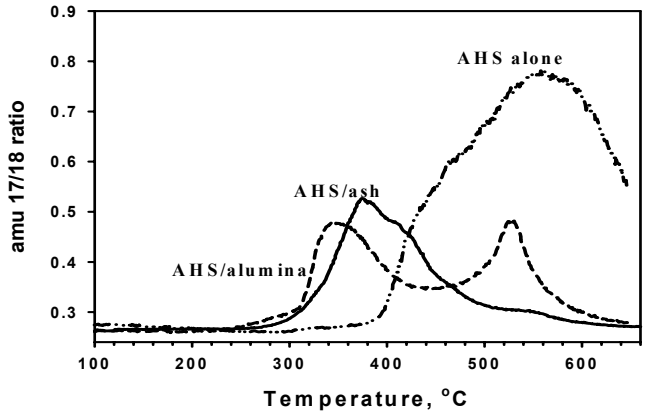

Figure 2. Ammonia evolution for AHS alone and blended with ash and alumina.

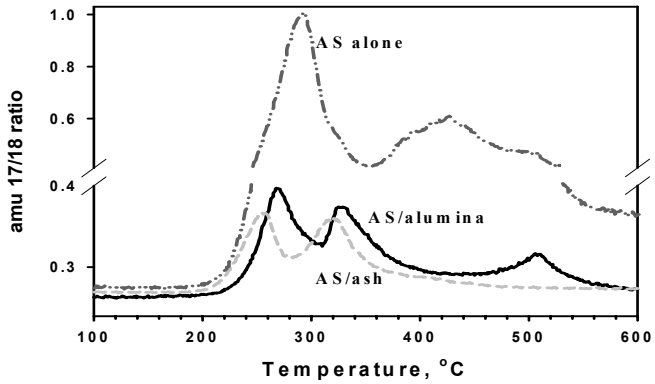

Figure 3. Ammonia evolution for AS alone and blended with ash and alumina.

ammonia evolution and weight loss profiles. The model matrices when subjected to TG-MS had weight losses of less than 0.2% which was related to surface moisture and no other evolved gases except for a small amount of high temperature SO_2 for the pre-heated ash. Therefore, weight loss and MS for the blends could be attributed to the inclusion of the ammonium salt. The ammonia release onset temperature, 260°C, was significantly lower for the mixes. Weight losses for the blends were spread over a longer duration with three pronounced steps detected for both model matrices indicating possible interactions between the decomposition products and the matrices. Mass transport considerations of the products passing through the matrix might also be a factor. SO_2 evolution occurred concurrent with ammonia except for the ammoniated alumina in which case SO_2 was detected after the ammonia release.

For the decomposition of AS, no difference in ammonia release onset was observed between pure and the blends. In all cases ammonia released occurred in three peaks, two major and one minor peak. Weight loss profiles were also similar with three steps. SO_2 evolution was not associated with the first peak of ammonia for AS pure or mixed with pre-heated ash but was detected with the second and subsequent release of ammonia. Similar to the AHS, SO_2 evolved after ammonia when AS was blended with alumina.

Comparisons of the SNCR, SCR, and FGC ashes with the salt/ash mixtures are shown in Figure 4 and 5. There was very good agreement of ammonia evolution for the SNCR and SCR ashes with ammonia evolution from the AS/ash and AHS/ash blends respectively (Figure 4). Ammonia evolution from the FGC ash occurred from 260 to 440°C encompassing portions of the temperature ranges for ammonia released observed for the SNCR and SCR ashes and corresponded best to the ammonia evolution profile acquired from a mixture of the AS/ash and AHS/ash blended together (Figure 5).

Conclusions

Comparison of TG-MS data for ammonia evolution from SNCR, SCR, and FGC ashes to the decomposition of AS and AHS salts, both pure and blended in alumina and ammonia-free ash suggested that the forms of ammonia captured in SNCR, SCR, and FGC were AS, AHS, and both AS plus AHS respectively. The ash matrix plays a significant role in the thermal characteristics of ammonia evolution.

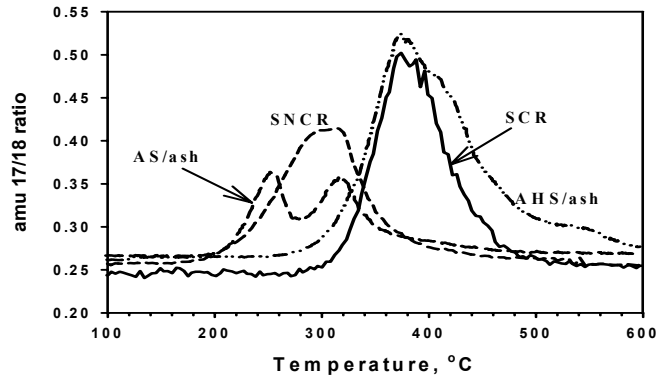

Figure 4. Comparison of ammonia evolution from SNCR and SCR ashes with ammonia release from salt/ash blends.

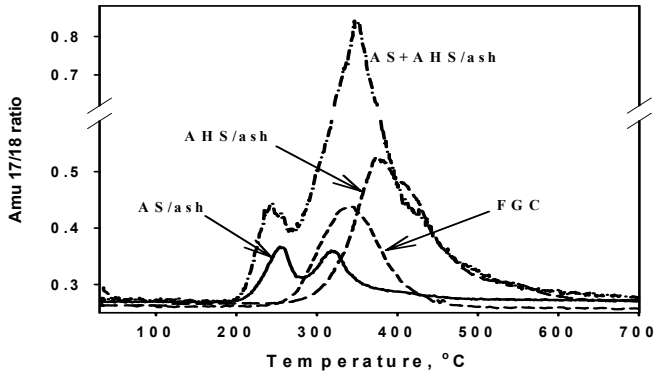

Figure 5. Comparison of ammonia evolution from FGC with ammonia release from salt/ash blends.

References

(1) Rubel, A M, Rathbone, R, Stencel, J. M. *Proc: 14th Internatl Sym on Mangmnt and Use of Coal Comb Prod (CCP's): Vol 1,* EPRI, **2001**, Palo Alto, CA:2001.1001158, p.9-1.

(2) Rubel, A.M., Stencel, J.M., Rathbone, B., *Internatl Ash Util Sym Proc,* **2001**, Lex, KY, CD ISBN 0967497132, paper 39.

(3) Rubel, A.M., Stencel, J.M., Rathbone, B., *19th Ann Internl Pitts Coal Conf Proc*, **2001**, Newcastle, NSW, Au, CD ISBN 1890977187, Session 40, paper 4.

(4) Eagan, M.L. and DuBois, L., Anal. Chim. Acta, **1974**, *70*,157.