

# Thermal Characteristics of Ammonia Release from Combustion Ash

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## ABSTRACT

Ammoniated ashes, received from two utilities employing either selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR), were studied using thermal gravimetry and mass spectrometry (TG-MS). They displayed significantly different temperatures at which ammonia began to evolve under thermal ramping conditions; these "onset" temperatures were 200°C and 280°C. The TG-MS data from the ashes were compared with TG-MS data from ammonia salts, including chloride, bisulfate and sulfate.

The differential weight loss from the TG data gave "peak" ammonia desorption temperatures of 320°C and 380°C. The "peak" and "onset" desorption temperatures suggested the form of ammonia on SCR and SNCR ashes were different. The coincidences and temperatures of ammonia and sulfur dioxide evolution during temperature ramping, and the ammonia decomposition rates were also examined. These and other molecular data are presented to define the thermal release properties of ammonia and to elucidate its speciation.

## Introduction

Characterization of ammonia incorporated into fly ash during SCR and SNCR usage by utilities enables evaluation of potential problems and solutions associated with its utilization and disposal. Ammonia has been described to be adsorbed onto unburned carbon on ash and incorporated as ammonium salts especially as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HSO}_4$ <sup>1-3</sup>. Ash, from utilities using SCR and SNCR processes, have different soluble adsorbed ammonia species,  $\text{NH}_4^+$  versus  $\text{NH}_3$ , suggesting different forms of adsorbed/absorbed ammonia which could relate to either or both the emission control process and the coal burned<sup>4</sup>.

TG-MS analysis has been found to be useful to study gas evolution and speciation from various materials<sup>5</sup>. We developed TG-MS methods to characterize coal and coal conversion by-products, particularly activated carbons<sup>6</sup>. Recently, our focus has been to apply TG-MS to characterize the forms of ammonia retained in combustion ash originating at coal-fired utilities using SCR and SNCR. In a previous study, a wide range of ammonia evolution

onset and peak temperatures ranging from 150° – 500°C and different rates of ammonia evolution were observed for eight different ashes<sup>7</sup>. The ammonia changed form with aging and, while some portion of the ammonia was adsorbed on unburned carbon, the major ammonia species on ash was not associated with carbon<sup>7</sup>. The current study was initiated to further define the thermal characteristics of ammonia release, particularly with respect to using either SCR and SNCR processes during coal combustion.

## Experimental

Two ashes were studied. They were obtained from two utilities, one employing SCR and the other SNCR. The ammonia concentration in each ash sample was determined by an ion selective electrode method<sup>8</sup>. Elemental analysis (C, H, N, and S),  $\text{SO}_4^{-2}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{PO}_4^{-2}$  anion concentrations by ion chromatography and loss on ignition (LOI) determinations were acquired.

TG-MS was done using a Netzsch Jupiter STA 449C thermal analyzer (TG) coupled to a Balzer Thermostar quadrupole mass spectrometer (MS). The two instruments are coupled via a heated fused silica capillary transfer line from the exit tube of the TG furnace to the MS detector. The ash sample size was between 100-200 mg. All samples tested were analyzed using a total flow of He of 80 ml/m metered at room temperature and pressure.

Two TG heating regimes were used. The ashes were first heated at a rate of 20°C/m to 900°C, and onset and peak temperatures of ammonia evolution were determined. Further characterization was done by heating the ashes at 20°C/m from room temperature to an isothermal heating period at temperatures near and at increments slightly above the onset temperatures, followed by heating at 20°C/m to 900°C. The rate of evolution of ammonia was determined from the differential of the weight loss (DTA) curve, which coincided with ammonia evolution as detected by MS.

Mass spectra were acquired either in histogram or in multiple ion detection (MID) modes. Spectra were acquired every 5 and 10 seconds. Identification of the evolution of ammonia versus water was determined by calculating the ratio of the MS signal for mass 17 (primary mass for ammonia) divided by the signal for mass 18 (primary mass for water).

## Results

The two ashes will be identified by the  $\text{NO}_x$  emissions control technology used in the power plants where they were generated. Table 1 gives the results of elemental, anion, and ammonia concentrations. The ammonia concentration of the ashes, as determined by the ion specific electrode method, was 680 and 338 ppm for the SCR and SNCR ashes, respectively. The carbon content was a

Table 1. Chemical characterization of study ashes

	SCR	SNCR
LOI	4.8	18.6
%C	0.9	33
%H	0.08	0.07
%N	<0.01	0.48
%S	0.9	0.3
%SO <sub>4</sub> <sup>-2</sup>	0.04	0.54
F <sup>-</sup> (mg/kg)	0.7	44
Cl <sup>-</sup>	0.67	17
NO <sub>3</sub> <sup>-</sup>	<0.01	14
Br <sup>-</sup>	<0.01	4
PO <sub>4</sub> <sup>-2</sup>	<0.01	34
NH <sub>3</sub> ↓	680	338
H/S	0.09	0.23
N/S	0.01	1.6
H/C	0.09	0.002
C/S	1	110

major difference between the two ashes, being less than 1% for SCR and 33% for SNCR.

Initial TG-MS analyses of these ashes indicated substantially different ammonia evolution onset and peak temperatures, 200°C and 320°C for SNCR and 280°C and 380°C for SCR. Ammonium salts with similar onset and peak evolution temperatures are NH<sub>4</sub>Cl, NH<sub>4</sub>HSO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Both ashes had very little Cl<sup>-</sup> and no detectable mass 35, the primary mass ion for Cl. Therefore, NH<sub>4</sub>Cl was not considered a significant contributor to the ammonia

captured by the ashes.

It was considered likely that the temperature of ammonia release from a salt in ash would be influenced by the ash's mineral component and therefore, different from the temperature of decomposition of a pure ammonium salt. However, similarities were still expected. Other factors, which have the potential to alter the ammonia release temperatures, are the evolution of other components of the ash during ammonia evolution, mass transport considerations, and heat transfer differences.

The ammonia evolution profiles from the two ashes determined from the intensities of the mass 17/18 ratio plotted versus temperature are shown in Figure 1. These profiles show the different evolution patterns of the two ashes including onset and peak temperatures. Clearly, there are different forms and/or release mechanisms for ammonia for the two ashes.

The decomposition rates of pure ammonium salts and the evolution rates of ammonia from the ashes were obtained from the dta curves. Comparison of the rates support possible influences of concurrent component release, mass transport, and heat transfer considerations. The decomposition rates of ammonium salts ranged from 3.3-to-8.3 e<sup>-2</sup>s<sup>-1</sup>; whereas, the ammonia evolution rates from the ashes were much slower, 6.8e<sup>-6</sup>s<sup>-1</sup> for SCR and 6.2e<sup>-6</sup>s<sup>-1</sup> for SNCR. The slightly slower rate for the SNCR ash is consistent with the evolution profile in Figure 1. These rates would include the influence of concurrently evolved components from the ash that may or may not be related to captured ammonia. Mass transport and heat transfer effects are consistent with the decreased evolution rates.

To further define the thermal characteristics of ammonia release from the ashes, they were subjected to isothermal heating at temperatures around their onset temperatures, which was followed by linear heating to 900°C. The two ashes responded very differently when subjected to this heating protocol. Figure 2 and 3 show the results for ammonia evolution for SCR ash. At onset temperatures, nearly 80 percent of the ammonia was released from the ash during the two-hour isothermal heating period. Only slightly more ammonia is released if the isothermal heating was continued for 8 hours or the isothermal heating temperature is increased up to 45°C above onset. The maximum rate of ammonia release averaged  $3 \text{ e}^{-6} \text{ s}^{-1}$  during both isothermal and ramp heating.

For the SNCR ash (Figures 4 and 5), only 40 percent of the ammonia was released after two hours of isothermal heating at onset temperature; increasing the isothermal temperature 45°C increased the amount of ammonia released to 69 percent. The maximum rate of ammonia evolution was  $2 \text{ e}^{-6} \text{ s}^{-1}$ , but the rate decreased to nearly zero within 30 minutes from the start of the isothermal heating. The maximum rate of weight loss from SNCR on ramping at the end of the isothermal period averaged  $5 \text{ e}^{-6} \text{ s}^{-1}$ .

Increasing the length of the isothermal period to 8 hours did not impact the amount of ammonia released. The weight loss from the SNCR ash during  $\text{NH}_3$  evolution at 230°C was the same as for a two-hour isothermal run (Figure 5). The weight loss during isothermal and ramping ammonia release from the ash were the same as for 2 hour isothermal heating. The rate of weight loss during ramping was similar for both the 2 and 8-hour isothermal runs. The weight loss from the SNCR ash during ammonia evolution may well be a function of other components of the ash being evolved concurrently with ammonia, as will be discussed later,  $\text{CO}_2$  and  $\text{NO}_x$  are also evolved from this ash during  $\text{NH}_3$  evolution.

The thermal analysis data clearly suggested that the forms of ammonia present in SCR and SNCR were significantly different, or ammonia release from the ash was impacted by the mineral and/or remaining evolvable components in the samples. Further insight into the possible differences in the form of ammonia was obtained from the MS data.

For both ashes, mass 64 ( $\text{SO}_2$ ), a major mass ion for  $\text{SO}_4$  decomposition, was detected during ammonia evolution during isothermal and ramp heating. Figure 6 shows evolution profiles for  $\text{NH}_3$  and  $\text{SO}_2$  for all isothermal temperatures, and Figure 7 provides an expanded view of the data acquired during ramp heating. There was concurrent evolution of  $\text{SO}_2$  and  $\text{NH}_3$  for the SNCR ash. The amount of  $\text{SO}_2$  evolved increased with temperature and there was a corresponding decrease in both  $\text{NH}_3$  and  $\text{SO}_2$  released during ramping as the isothermal temperature was increased. In the SCR case, evolution of  $\text{SO}_2$  occurred only at the highest isothermal temperature. During ramping,  $\text{SO}_2$  evolved as a shoulder on a much larger  $\text{SO}_2$  peak, which had a maximum at 600°C (Figure 7).

The other masses detected during or near ammonia evolution were those associated with CO<sub>2</sub> and NO<sub>x</sub>. Figure 8 gives the evolution profiles for CO<sub>2</sub>, with respect to NH<sub>3</sub> evolution, and Figure 9 shows the expanded ramping data. The release of CO<sub>2</sub> from SNCR presented a similar situation to SO<sub>2</sub> release and showed CO<sub>2</sub> release, which directly correlated to NH<sub>3</sub> release during the isothermal and post isothermal ramping. For the SCR ash, there was no concurrent evolution of CO<sub>2</sub> but CO<sub>2</sub> did evolve immediately after NH<sub>3</sub> release was complete. These results may have some implications for NH<sub>3</sub> capture but may also reflect the fact that the amount of residual carbon in the SCR ash was very low in comparison to the SNCR ash. The release of NO<sub>x</sub> during or near NH<sub>3</sub> evolution followed the same pattern as CO<sub>2</sub> except for heating to the highest isothermal temperature, 325°C, for the SCR ash, where some NO<sub>x</sub> was released concurrent with ammonia. Otherwise, no NO<sub>x</sub> was detected until after NH<sub>3</sub> evolution was completed. In the SNCR case, there was concurrent release of NO<sub>x</sub> with all isothermal temperatures used.

## Discussion and conclusions

These data for ammonia evolution from the two ashes suggest that ammonia captured by the SCR ash was probably in a sulfate form. The TG-MS data from a (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> salt indicated a delayed detection of SO<sub>2</sub> when it decomposed similar to the evolution profile of SO<sub>2</sub> from SCR. Since the SCR ash had a residual carbon content of less than 1%, it is highly unlikely that carbon played a role in the storage of ammonia; further evidence for this conclusion was the fact that no CO<sub>2</sub> evolved simultaneously with NH<sub>3</sub> evolution. In the SNCR case, the lower onset and peak temperatures for NH<sub>3</sub> evolution coupled with a much higher SO<sub>4</sub><sup>-2</sup> concentration would be consistent with all or part of the ammonia being in the form of NH<sub>3</sub>HSO<sub>4</sub>. However, a role for residual carbon affecting ammonia storage cannot be ruled out for the SNCR ash. It had a high residual carbon content, 33%, and CO<sub>2</sub> was evolved with NH<sub>3</sub>.

The differences, in the rate of ammonia evolution between the two ashes probably, reflects differences in the concurrently evolved gases and in heat transfer and mass transport effects related to the mineral components of the ash. During the isothermal runs, the maximum rate of ammonia evolution for SCR was the same during the isothermal and ramp heating, suggesting one mechanism of ammonia release. However, in the SNCR case, an increase in the rate of evolution during post isothermal ramping suggested a reduction of the energy required to maintain NH<sub>3</sub> storage on the ash during isothermal heating, or even two storage mechanisms.

The TG-MS results for the two samples provide sufficient data for definitive conclusions as to the differences in the forms and mechanisms of ammonia storage. They also indicate that substantial differences are possible, and are likely, depending on the coal and/or the NO<sub>x</sub> emissions control process used

during coal combustion and ash formation. These data start to define these differences. Only with the analysis of more samples will a definitive elucidation of the mechanisms and vehicles of ammonia storage in ash be possible.

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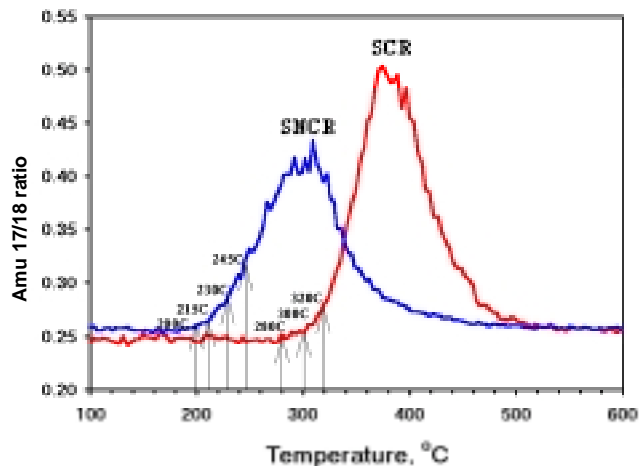


Figure 1. Ammonia evolution profiles for SCR and SNCR ashes

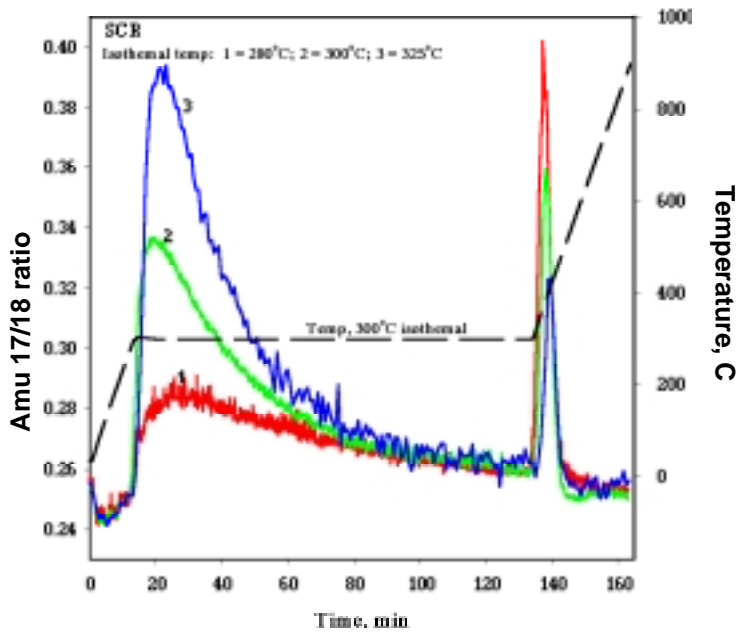


Figure 2. Ammonia evolution for SCR ash during isothermal and ramp heating

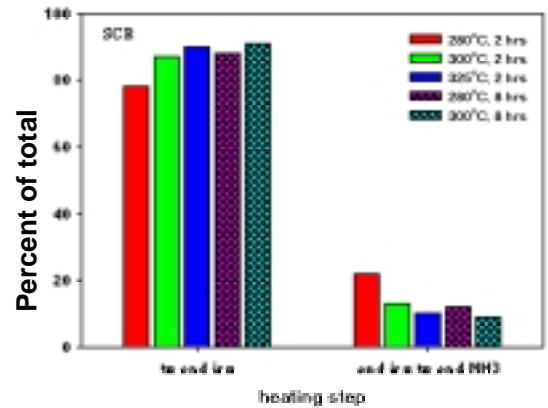


Figure 3. Percent weight loss during ammonia evolution from SCR ash during isothermal and ramp heating

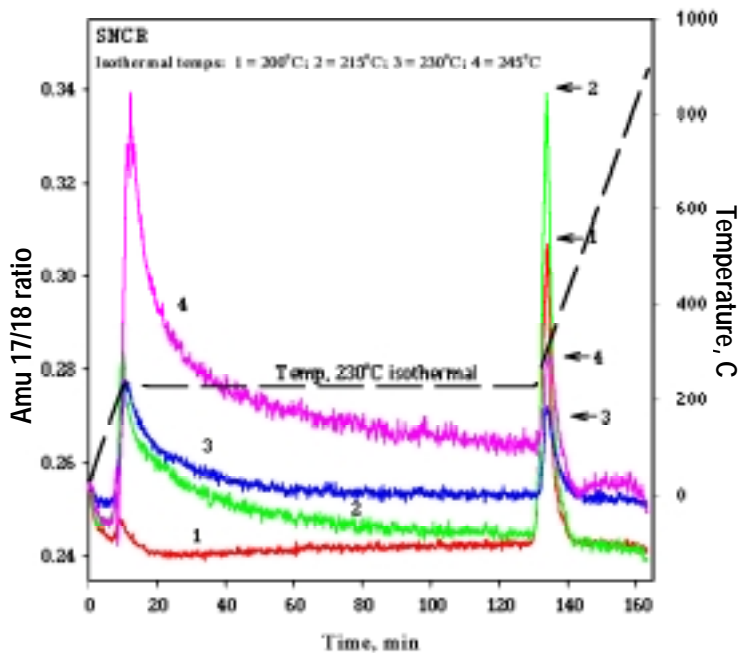


Figure 4. Ammonia evolution for SNCR ash during isothermal and ramp heating

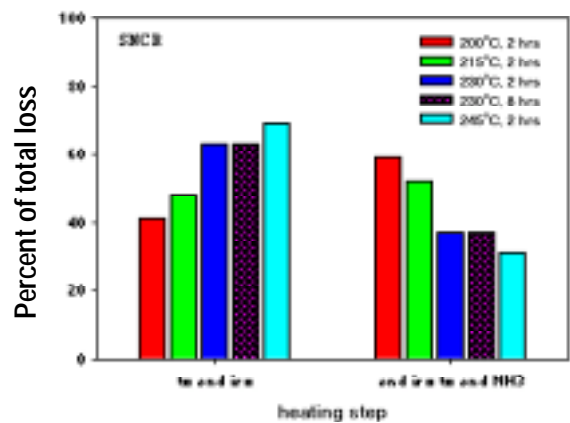


Figure 5. Percent weight loss during ammonia evolution from SNCR ash during isothermal and ramp heating

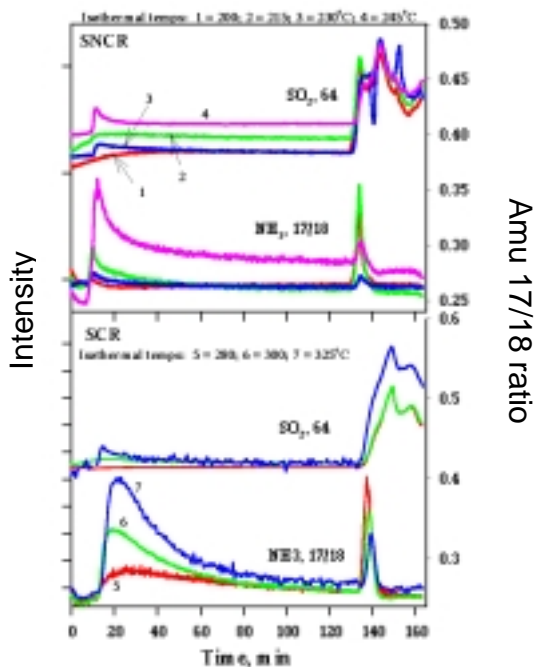


Figure 6. Evolution profiles for NH<sub>3</sub> and SO<sub>2</sub> for SCR and SNCR ashes for isothermal and ramp heating

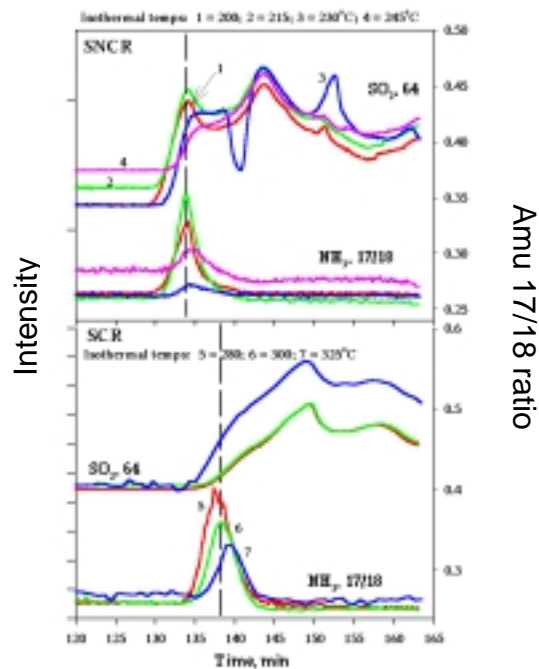


Figure 7. Evolution profiles for NH<sub>3</sub> and SO<sub>2</sub> for SCR and SNCR ashes for ramp heating

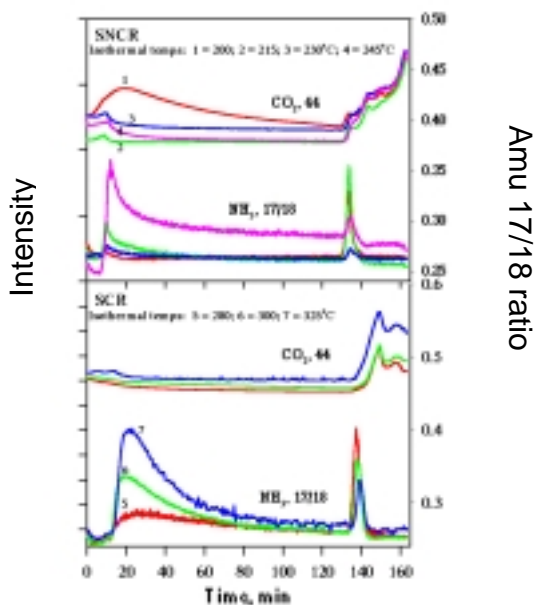


Figure 8. Evolution profiles for NH<sub>3</sub> and CO<sub>2</sub> for SCR and SNCR ashes for isothermal and ramp heating

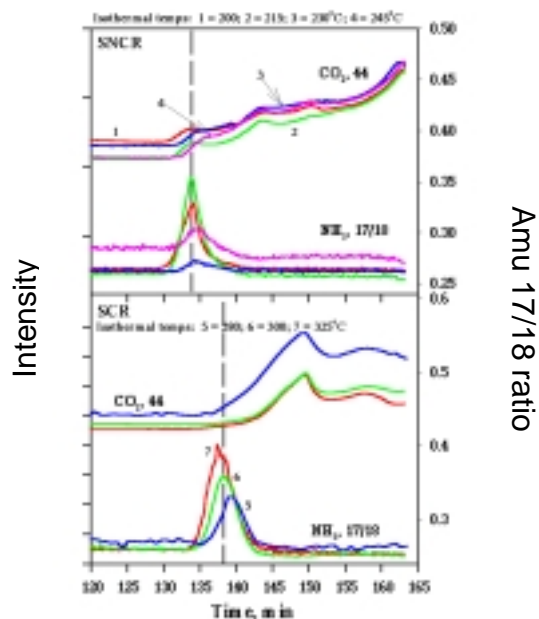


Figure 9. Evolution profiles for NH<sub>3</sub> and CO<sub>2</sub> for SCR and SNCR ashes for ramp heating