Release of Ammonia from SCR / SNCR Fly Ashes

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KEYWORDS: fly ash, ammoniated fly ash, leaching

Abstract

One of the goals of the Department of Energy is to increase the utilization of coal utilization byproducts (CUB) to 50% by 2010. This will require both developing new markets and maintaining traditional ones such as the use of fly ash in concrete. However, the addition of pollution control devices can introduce side-effects that affect the marketability of the CUB. Such can be the case when NO_x control is achieved using selective catalytic or non-catalytic reduction (SCR or SNCR). Depending on site-specific details, the ammonia slip (un-reacted NH_3 which is carried down-stream in the flue gas) can cause elevated levels of NH_3 in the fly ash. The odor alone can be sufficient to adversely affect marketability. Disposal of ammoniated fly ash can present environmental concerns related to the amount of ammonia that might be released, the amount of water that might become contaminated, and the extent to which metals might be mobilized by the presence of the ammonia. This poster describes the column leaching of ammoniated fly ashes. It provides quantitative measurements of the total amount of ammonia released from a selection of ashes and the amount of water needed to exhaust the ammonia supply. It also considers the mobilization of metals caused by the ammonia.

Introduction

One of the goals of the Department of Energy is to increase the utilization of coal utilization byproducts (CUB) to 66% by 2010. This will require both developing new markets and maintaining traditional ones such as the use of fly ash in concrete. However, the addition of pollution control devices can introduce side-effects that affect the marketability of the CUB. Such can be the case when NO_x control is achieved using selective catalytic or non-catalytic reduction (SCR or SNCR). Depending on site-specific details, the ammonia slip (un-reacted NH_3 which is carried down-stream in the flue gas) can cause elevated levels of NH_3 in the fly ash. The odor alone can be sufficient to adversely affect marketability. Disposal of ammoniated fly ash can present environmental concerns related to the amount of ammonia that might be released, the amount of water that might become contaminated, and the extent to which metals might be mobilized by the presence of the ammonia.

Experimental

Plant personnel collected all of the samples. Ashes were obtained from a number of sources and included ashes from units using both SCR and SNCR technologies. In some cases, it was possible to obtain ashes from the same facility both with the pollution control device on-line and off-line.

A liquid chromatography column was filled with a slurry containing 100g of fly ash in 200 ml of Milli-Q® water. Leachate was collected by draining the column until the water meniscus touched the top of the ash. The maximum drip rate was controlled using the outlet stopcock so that elution times were at least a couple of hours. For low-permeability ashes, elution sometimes continued overnight. Additional 100 ml portions of water were added, eluted and collected until the ammonium in the leachate was below 10 mg/L. In practice, it was never necessary to add more that 3 additional 100-ml portions of water. The eluant was collected in capped vessels that contained one ml of trace-metal grade HCl to prevent ammonia loss. The caps were drilled to allow the tip of the column to enter with minimal clearance. Ammonium in the leachates was measured using an ammonia selective ion electrode after adjusting the pH to > 12. Metals in the leachates were determined using ICP-OES. Mercury was determined using CVAA.

Results and Discussion

None of the as-received fly ashes exhibited the odor of free ammonia. Ammonia determinations before and after exposure to the atmosphere, or even before and after overnight heating to 100^{o}C, were identical. It appears that all of the ammonia in these samples is present either as ammonium salts[1] or perhaps as NH_3 chemisorbed to the fly ash carbon.[2] The following discussion will take the former point of view as a convenience for discussion with the realization that the leaching of chemisorbed NH_3 has not been discounted.

Ammonium was always most concentrated in the first 100 ml of leachate and the total amount eluted correlated well with this initial concentration as can be seen in Figure 1. The slope of the best-fit line in Figure 1 is 1.3 indicating that about 75% (1/1.3) of the ammonium elutes in the first fraction. And, on average, another 25% elutes in the subsequent fractions. As can be seen in Table 1, the amount of ammonia in the first 100 ml of leachate ranged between 0.5 and 400 mg/L and the total amount leached ranged from about 1 to over 500 mg ammonium per kilogram of ash. These statistics are for the entire set of 27 samples. Statistics for two sub-sets of the data are shown in Table 2. These subsets represent samples from 10 different power plants. Ten samples were taken with the pollution control devise on-line and 10 with the devise off-line. The amount of ammonium leached from the samples taken with the control devise on-line was always higher than without the devise although the decrease was not always large, especially for those ashes that had low ammonium concentrations in both cases. Determinations of the total, rather than leachable, ammonium were not made but the results of Wang *et al.* would indicate that recoveries in the range of 70-90% might be expected.[3]

The relationship, or lack thereof, between the ammonium leached from the fly ash and the amount of some trace metals in the leachate are shown for mercury, chromium and zinc in Figures 2, 3, and 4. The two ashes that released the most ammonium (ca. 400 mg/L) consistently gave some of the lowest amounts of metals in the leachate. Mercury values ranged from less than 1 to a little over 200 parts per trillion and showed no trend with ammonium. Most surprising was the fact that chromium in the leachate showed no strong relation to the amount of ammonium because ammonia has been found to enhance the recovery of Cr from municipal fly ashes.[4]

Conclusions

Ammonia captured in fly ash appears to be present as either an ammonium salt or as a chemisorbed species. Leachable ammonium was usually below 200 mg/kg but approached 500 mg/kg in two cases. Most of the leachable ammonium was removed in the first batch of leachate. Metals, though present in the leachates, showed no correlation to the amount of ammonium present.

References

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Statistic	First Fraction (mg NH_3 / L leachate)	Total Amount (mg NH_3 / kg ash)
Min =	0.48	0.91
Max =	400	527
Mean =	60.43	86.09

Table 1. Statistics describing the ammonium leached from a selection of coal fly ashes.

Statistic	**With Control Devise On-line**	
	First Fraction (mg NH_3 / L leachate)	Total Amount (mg NH_3 / kg ash)
Min =	3.0	5.1
Max =	100.0	117.0
Mean =	33.1	45.0

Statistic	**With Control Devise Off-line**	
	First Fraction (mg NH_3 / L leachate)	Total Amount (mg NH_3 / kg ash)
Min =	0.5	0.9
Max =	20.0	26.0
Mean =	4.4	6.1

Table 2. Statistics describing the ammonium leached from subsets of the fly ashes in Table 1.

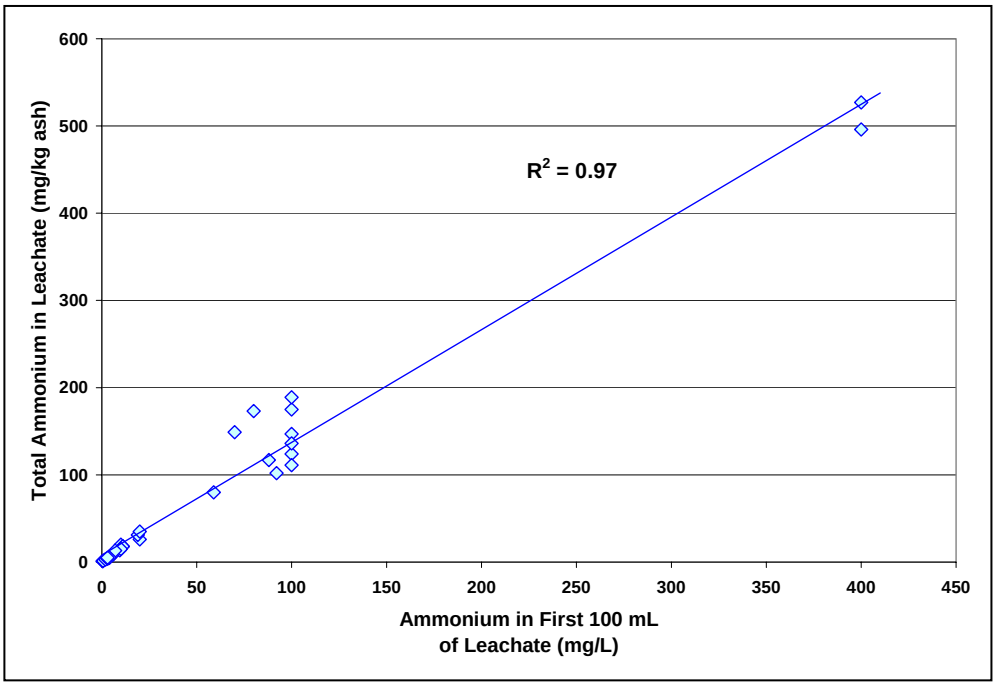

Figure 1. Relation of Total Ammonium Leached (mg ammonium / kilogram of ash) to the Concentration of Ammonium in the First 100 ml of Leachate mg ammonium / liter leachate).

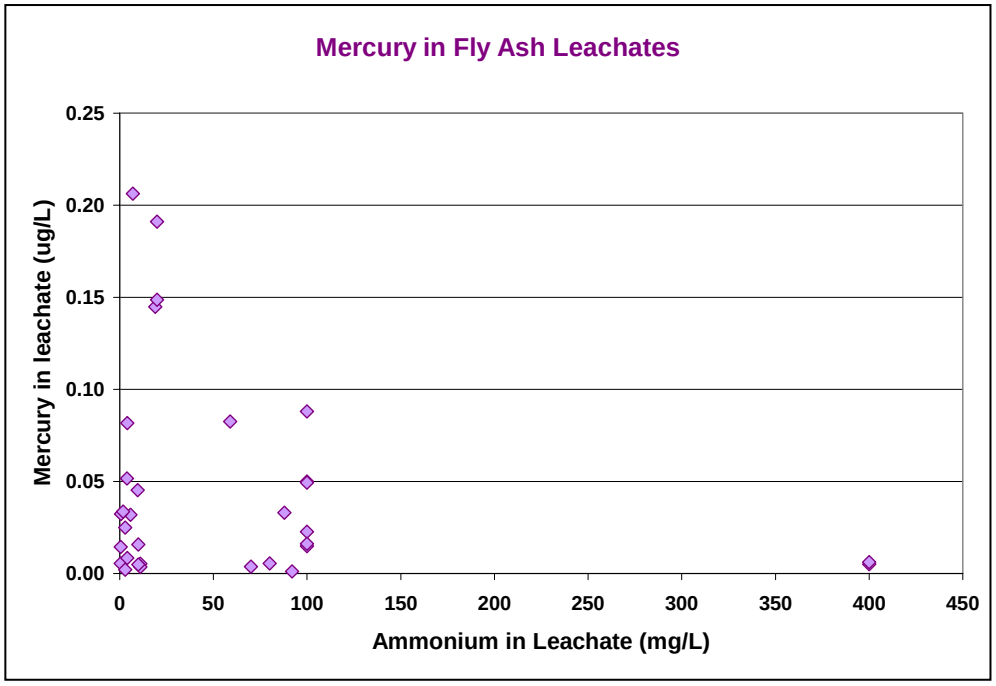

Figure 2. Relation of the amount of mercury in the fly ash leachate to the ammonium.

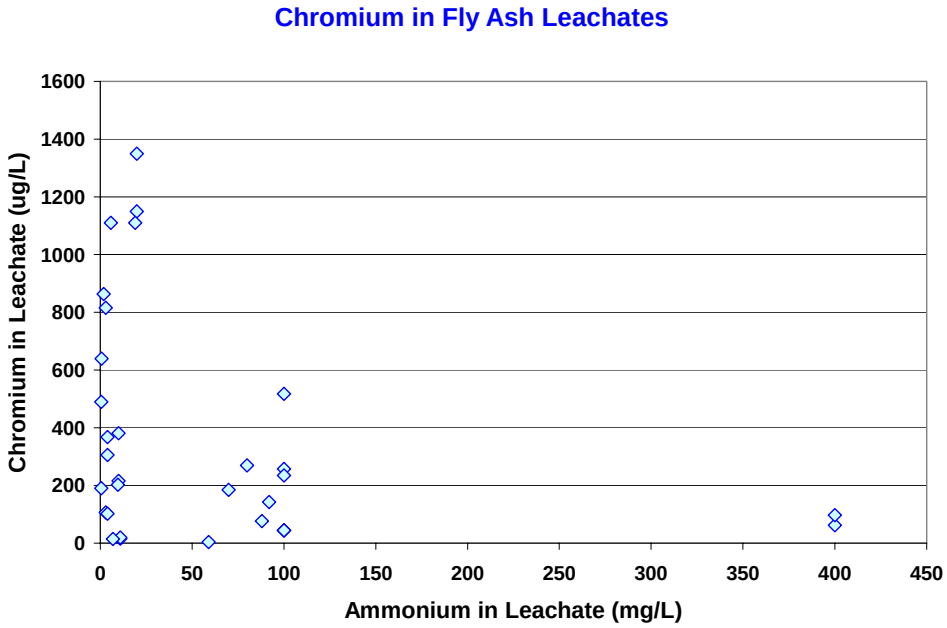

Figure 3. Relation of the amount of chromium in the fly ash leachate to the ammonium.

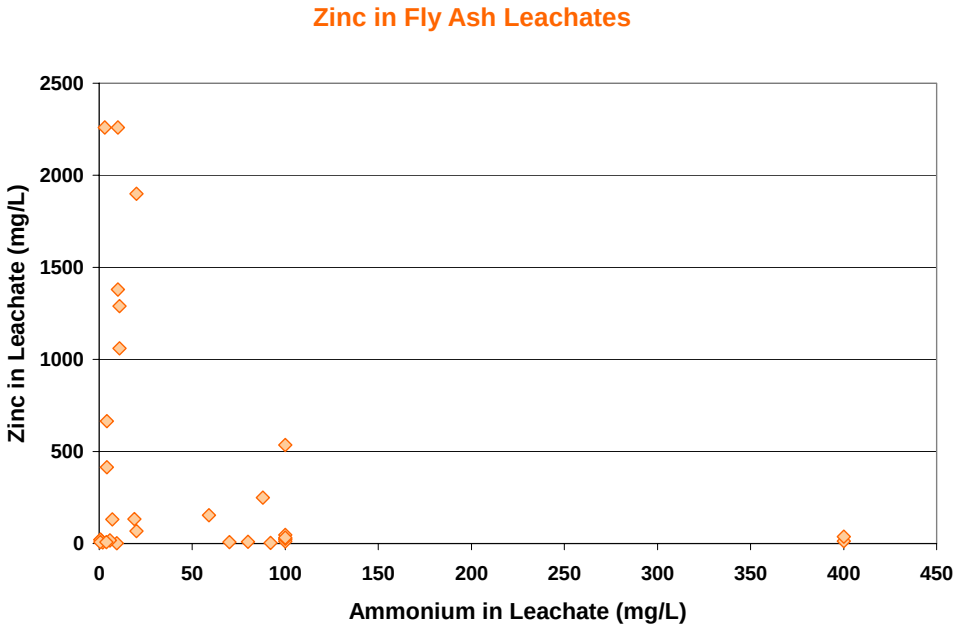

Figure 4. Relation of the amount of zinc in the fly ash leachate to the ammonium.