

Removing Ammonia from Fly Ash

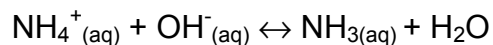
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Ammonia Contaminated Fly Ash

The supply of fly ash available for use as a pozzolan in concrete may be severely impacted by the effects of air quality regulations on utility plant operations.¹ Specifically, mandated reductions in NO_x, particulate, and SO₃ containing aerosol emission levels are expected to require the installation of control systems which may use ammonia as a reagent. Depending on the level of ammonia present in the flue gas at the unit precipitators, the collected fly ash may be heavily contaminated with ammonia primarily as ammonium sulfate salts^{1,2}. For NO_x control, the flue gas ammonia level will be set by the amount of ammonia “slip”, i.e. unreacted ammonia present after the SCR or SNCR unit. For precipitator enhancement to reduce particulate or SO₃ aerosol emissions, ammonia is injected into the flue gas prior to the precipitators and will be deposited on the fly ash. The degree to which this occurs is dependent on the SO₃ content, fly ash sulfur content, alkalinity of the fly ash, the ammonia concentration, and ash loading in the flue gas.

The use of fly ash in concrete requires that the fly ash have specific physical and chemical properties³. The pozzolanic properties of the ash are activated in the concrete by the generation of highly alkaline free lime from hydration of the cement. When fly ash contains ammonia, this ammonia is liberated as a gas by the action of the highly alkaline solution of the concrete. The alkalinity shifts the equilibrium of ammonium ion in solution to molecular ammonia according to the following equation:



The dissolved molecular ammonia is easily released from solution as free ammonia gas.

Ammonia is a strong smelling compound that carries the connotation of barnyards, manure and urine. A strong odor of ammonia is unacceptable to the concrete producer, the contractor working with the concrete, and the ultimate concrete user.⁴

The finished properties of the concrete are not adversely affected when using ammonia contaminated fly ash, but the odor is unacceptable, particularly if the concrete is used in underground or enclosed spaces.^{5,6,7} Depending on the specifics of the location, including the amount of fresh air circulation, ammonia odor was found not to be objectionable when using fly ashes containing 100 to 200 mg NH₃ / kg (part per million by weight, or ppm). In order to assure that no problems are encountered, the ammonia content of fly ash should be no greater than 100 ppm^{2,8}.

However, the addition of ammonia at the power generation plant can result in fly ash ammonia contents of 200 to 2500 ppm, rendering the fly ash unacceptable for use in concrete.⁹ Thus, reducing air quality problems by controlling the air emissions of power plants increases a solid waste disposal problem and increases CO₂ greenhouse emissions by increasing the amount of cement used in concrete production. Removal of ammonia from fly ash so that it can be used in concrete would benefit the utility by avoiding solid waste disposal, the concrete producer, user, and ultimate owner by lowering the cost of materials and increasing product quality, and the environment by reducing emissions of greenhouse gases from cement production.

The amount of ammonia and ammonium salts found in fly ash is related to the amount of ammonia present in the flue gas. For a typical pulverized coal unit using eastern bituminous coal with a high heating value of 12,000 BTU/lb, the flue gas to coal mass ratio is approximately 8 to 9.5. When the ash content of the coal is 10%, and 80% of the ash in the coal is recovered as fly ash (20% to bottom ash), the flue gas / ash ratio is approximately 100. If all of the ammonia species present in the flue gas were deposited or adsorbed on the fly ash, the concentration of the ammonia in the ash would be approximately 50 times greater than in the flue gas on a mass basis, e.g. an ammonia "slip" of 2 ppm by volume would result in an ash containing 100 mg / kg (ppm by wt.) ammonia. Actual measurements show this relationship to be correct.¹⁰ The concentration of ammonia on fly ash will vary among operating units dependent on the ash content of the coal and the fly ash to bottom ash ratio as well as other factors.

Ammonia injection to electrostatic precipitators (ESP) to improve efficiency and reduce plume opacity can result in very high levels of ammonia in fly ash. Levels up to 2500 ppm ammonia in ash have been found for such systems. SNCR operations typically operate with ammonia slip concentrations of 5 to 20 ppm, with ash contaminated to a level of 200 to 1000 ppm ammonia. SCR systems generally are designed to operate at maximum ammonia slip levels of 2 or 5 ppm, depending on the specifics of the installation.¹¹ Generally, the greater the NH₃/NO_x ratio, the greater the NO_x reduction which will be obtained, with a higher ammonia slip resulting. However, ammonia slip greater than 2 ppm may result in ash-ammonia contents of greater than 100 ppm, producing an unmarketable ash.¹² Many power plants in Japan and Germany operating SCR units designed for a 2 ppm maximum slip have seen little impact on the marketability of fly ash.^{1,5} However, some SCR's around the world and in the U.S. are being designed for 5 ppm ammonia slip. These units will have problems with greater than 100 ppm of ammonia on the fly ash.

Controlling ammonia slip to low levels also reduces plugging and corrosion of downstream equipment due to deposition of ammonium sulfates.^{1,10} Avoiding air preheater plugging due to this phenomena is expected to be even more important to unit operators when burning high sulfur, US coals. Thus, management of ammonia slip to minimize unit outage time will be a greater concern than controlling the ammonia level of fly ash. The result may be that no significant problem develops for the utilization of ash at some utility sites, depending on the specific design and operation of the emission control systems.

Other ammonia removal / treatment processes

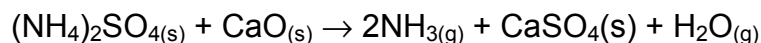
Many processes have been proposed and patented to remove ammonia from fly ash. Thermal processes have been proposed to desorb / decompose the ammonia salts between 300 to 500° C (550 - 900°F).^{4,13,14,15} This is an obviously energy intensive process. A variety of methods utilizing water extraction or reaction of the ammonia salts with alkaline water have been examined.^{16,17,18} These processes typically result in ash with very high alkali content, 5 to 40% of the original mass of ash, which would alter the ash chemistry significantly and limit its use as a pozzolan in the production of concrete. Also, these processes often require large quantities of water, 10 to 50%, which must be removed from the fly ash, requiring uneconomical drying steps.^{16,17,18}

The STI Process

STI has patented a process that removes ammonia from fly ash.¹⁹ The process recovers 100% of the fly ash treated and the resulting ash meets all specifications for use in concrete. STI's ammonia removal process can be used alone or in combination with the company's carbon separation technology. The carbon separation process is not affected by the presence of ammonia. This modular approach offers the lowest cost solution for treating otherwise unusable fly ash.

To remove ammonia as a gas from the fly ash, the STI process utilizes the same fundamental chemical reaction that results in ammonia release in concrete. Liberation of ammonia from fly ash requires that the ammonium ion - molecular ammonia equilibrium be shifted in favor of ammonia by the presence of alkali. Fly ashes with naturally high alkalinity need no additional alkali. For less alkaline ashes, any strong alkali will serve. The cheapest source of alkali is lime (CaO). The reaction of ammonium salts with lime liberating ammonia is strongly favored by chemical equilibrium. The chemical reaction occurs rapidly once the compounds are dissolved.

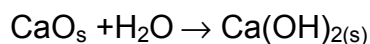
The overall reaction can be generalized as:



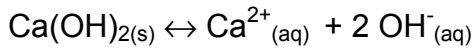
However, the vapor pressures of the solids are quite low and the reaction cannot occur in the gas or solid phase. Ammonium sulfate is highly soluble in water and dissociates to ammonium ions and sulfate ions.



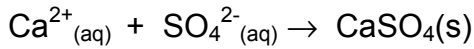
Lime is highly unstable on exposure to water, favoring a highly exothermic reaction commonly known as "slaking", producing calcium hydroxide or hydrated lime.



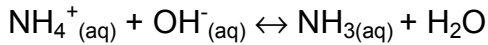
The hydrated lime is only sparingly soluble in water, producing calcium and hydroxide ions.



Calcium sulfate is also sparingly soluble, so as calcium ions are made available by dissolving the hydrated lime, they are primarily consumed by precipitation of calcium sulfate.



Finally, an equilibrium exists between ammonium ions and ammonia dissolved in water.



The degree to which ammonium ions are converted to molecular ammonia is dependent on the pH of the aqueous system, higher pH's favoring the formation of molecular ammonia. This equilibrium is well known.²⁰

A key feature of the STI process is the use of a minimum quantity of water (1 to 4%, typically 2%) and minimal quantities of alkali (< 2%). Large amounts of water are detrimental to the process, slowing the rate of ammonia release. The pH of the resulting ash / lime / water mixture should be greater than pH 10.0. Very small quantities of alkali are added to assure this pH, depending on the natural pH of the ash. Typically, less than 1% Ca(OH)₂ is required, even with fly ash with naturally acidic pH. Calcium based alkalis are used which result in minimal alteration of the fly ash chemistry. The process is performed at ambient temperature.

Figure 1: Ammonia Release from Fly Ash

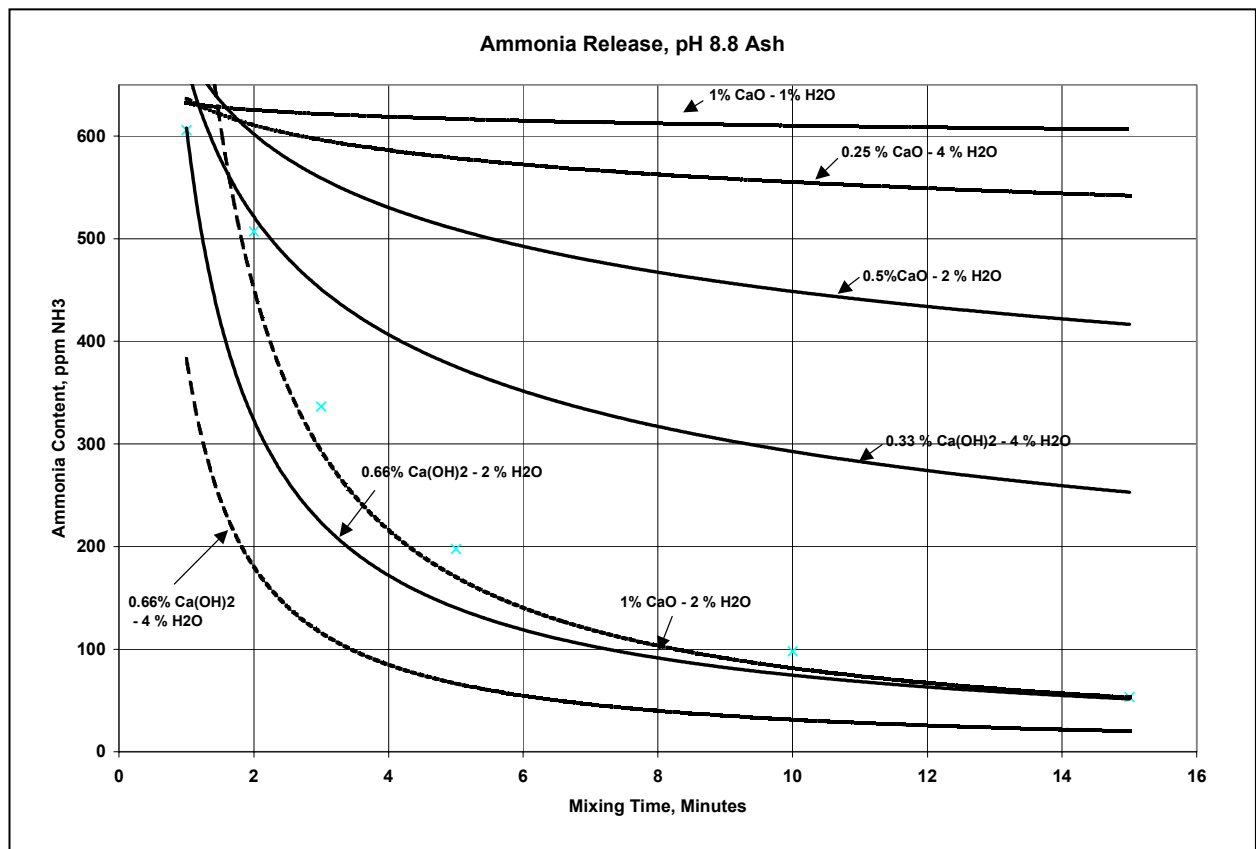
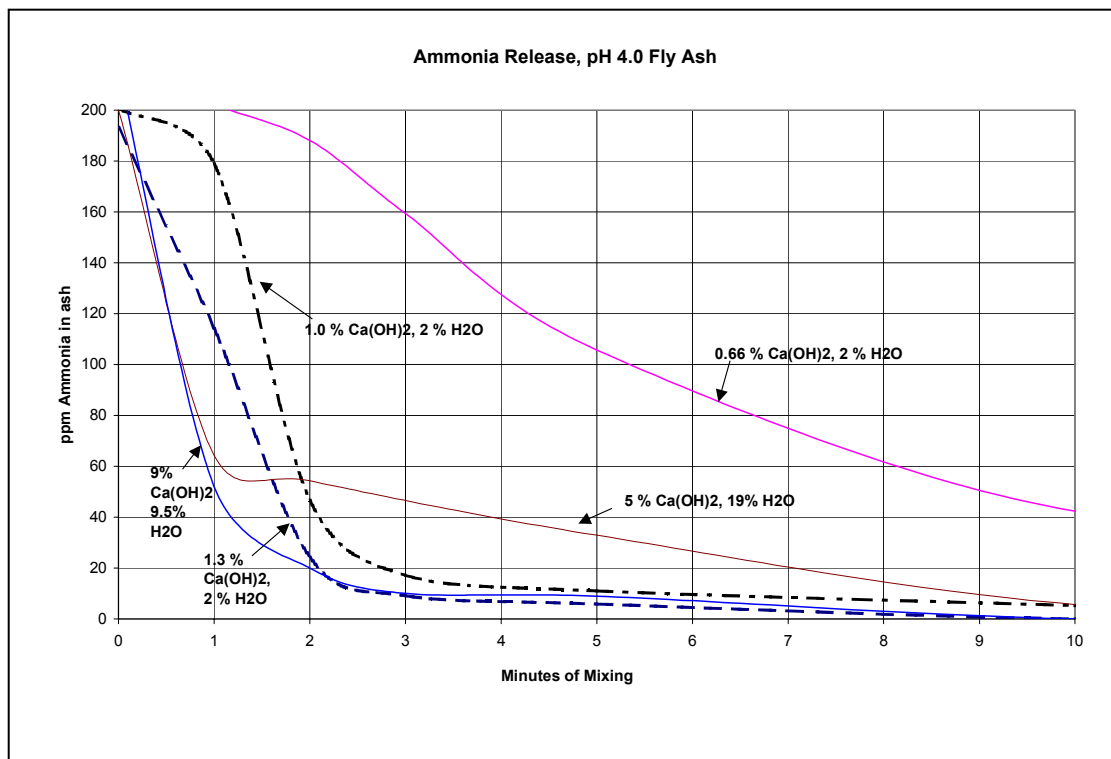


Figure 1 illustrates the effects of water and alkali addition on the removal of ammonia from an ash initially containing 650 mg / kg ammonia. The most rapid loss of ammonia results from a careful balancing of water and alkali addition. Excess alkali does not aid evolution if insufficient water is present and vice versa. The case using 1% CaO and 1% H₂O results in very little evolution of ammonia, while 1 % CaO and 2% H₂O is very effective in removing ammonia. More interesting is the effect of the type of alkali material added to the ash. The addition of 0.5% CaO with 2% H₂O provides an equivalent amount of alkali to the system as 0.66% Ca(OH)₂ and 2% H₂O. However, the calcium hydroxide results in a much faster ammonia removal. The phenomenon is due to the elimination of the relatively slow "slaking" reaction in which CaO hydrates to form Ca(OH)₂, and the consumption of water in that reaction. High rate of ammonia release is obtained by creating a surface film of sufficient alkalinity to shift the ammonium ion - ammonia molecular equilibrium to favor formation of volatile ammonia. Using minimal water results in a high concentration of ammonia in the water film maximizing the evolution rate of ammonia from solution.

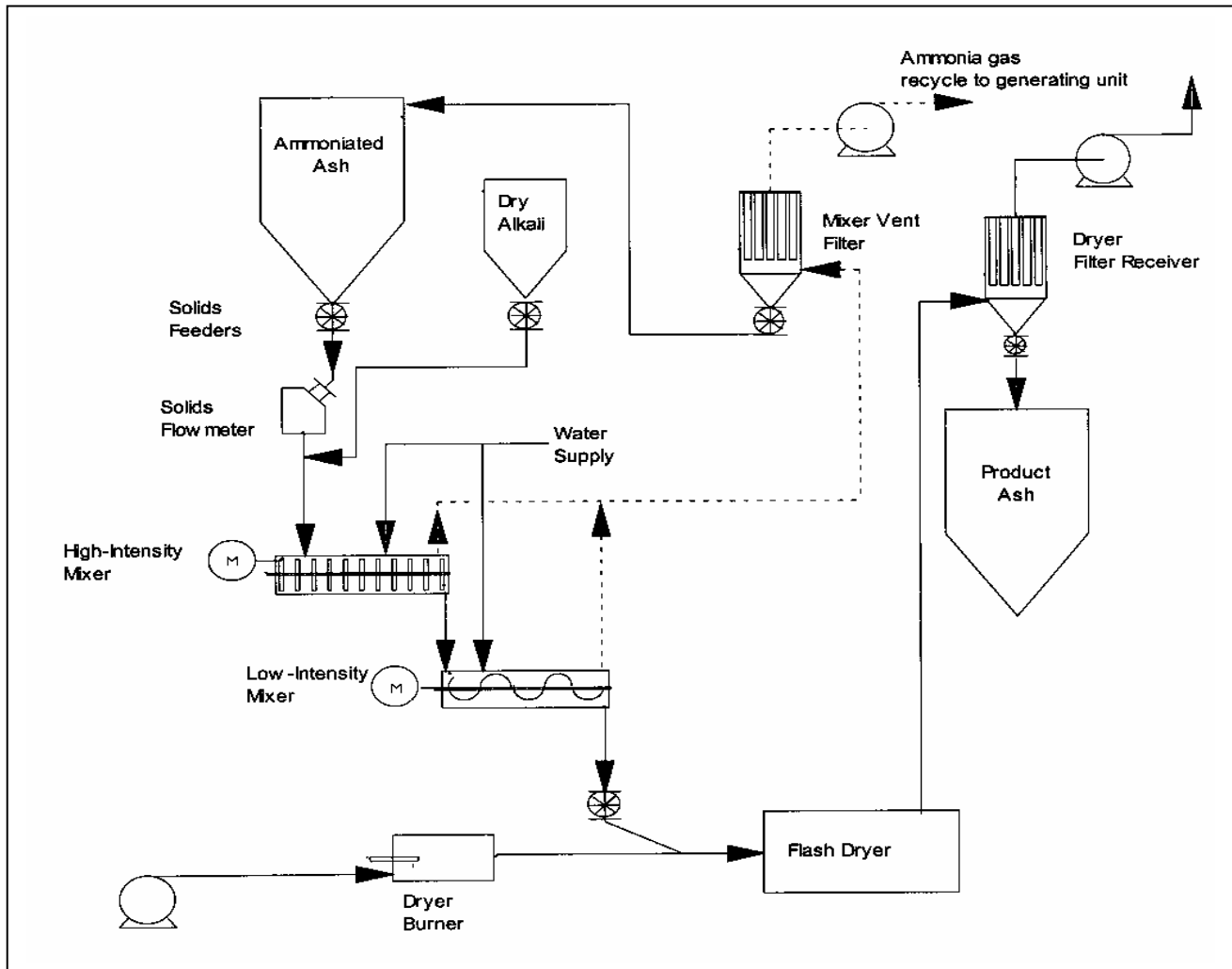
Figure 2 further shows the effect of water and alkali dosage. In this case, the natural pH of the fly ash is low: pH 4.0, and an initial ammonia concentration of 200 mg / kg. This requires a somewhat greater amount of alkali than the previous case to have a rapid release of ammonia. However, high amounts of lime and water do not result in significantly faster ammonia release. In fact, using 19% water results in a substantially slower release of ammonia after a short period, even with relatively high Ca(OH)₂ addition.

Figure 2: Effect of High Water Content



Since the cost of the alkali and cost of drying the product are major operating expenses and sizing the mixing and drying equipment are the major components of capital cost, carefully measuring the reagent requirements for a specific ash is necessary to optimize the economics of the process.

Figure 3: STI Ammonia Removal Process Flow Diagram



The process flow diagram for the continuous operation of the STI process is presented in Figure 3. Ash, water and alkali in controlled proportions are metered to a mixer. To assure rapid mixing and uniform dispersion of the added water and alkali, a high intensity mixer is used. The residence time in this type of mixer is very low - on the order of one second. Ammonia is immediately released but complete evolution requires mixing times of 3 to 4 minutes. To obtain this mixing time and assure good transport of the ammonia from the bulk of the ash, a low intensity device such as a pug mill is used as a secondary mixer. Since the moisture content of the ash is very low, the material flows through this mixer as a highly agitated dry powder. Ammonia gas collected in both the high and low speed mixers is recycled to the generating unit flue. Recycling the collected ammonia gas reduces ammonia addition to the flue and minimizes ammonia emission to the environment.

The deammoniated ash is dried by conveying the material through a flash drier to remove excess water. Due to the minimal amount of water added, water consumed in the formation of hydrated calcium sulfate upon reaction with soluble sulfate in the ash,

and loss of water during the low intensity mixing stage, only a small amount of water needs to be removed by the drier. This minimizes the energy demand of the drying stage. Final ash temperatures of approximately 150°F are adequate to produce a completely free-flowing, product fly ash with moisture contents well below the ASTM C 618 specification of 3 wt. %.³

In pilot plant trials conducted by STI, the continuous process has reduced the ammonia concentration of contaminated ash containing up to 1000 mg NH₃ / kg to less than 20 mg NH₃ / kg at a rate of 3000 lb/hour. Design of a commercial size operation is underway which will handle 40 tons per hour of contaminated ash. The process is scalable to handle more than 100 tons per hour of ash using commercially available, non-proprietary equipment.

The Product Ash

The recovered fly ash meets all chemical and physical requirements of the ASTM C 618 standard and resulting concrete properties are identical to ash not subjected to the ammonia removal process. Table I compares typical properties of ash from one generating station along with properties of the plant ash reduced in ammonia content from 250 mg / kg to 20 mg / kg by the continuous STI process. Note that the range of calcium oxide content observed for the ash from this source is 1.4 to 12%. The addition of up to 1% Ca(OH)₂ (0.75% as CaO) will result in only minor changes in the ash chemistry, broadening the variability insignificantly.

Concrete testing performed on the deammoniated ash showed it to be an excellent pozzolanic material. Compressive strength development using this ash is as good as or better than unammoniated ash from this source. Long term concrete durability properties are also excellent, including improved corrosion resistance, sulfate resistance, chloride permeability, and lime shrinkage.

Table I: Fly Ash Physical and Chemical Properties.

	ASTM C 618 specification	Plant # 1 Ash Properties, Typical	Plant # 1 Ash After Ammonia Removal
Chemical Composition			
Silicon Dioxide	-	55 - 61 %	59.8 %
Aluminum Oxide	-	15 - 25 %	23.8 %
Iron Oxide	-	5 - 10.9%	7.35
Total (SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃)	70.0 Min.	78 - 91 %	90.9 %
Sulfur Trioxide	5.0 Max	0.13 - 1.4%	0.87%
Calcium Oxide	-	1.4 - 12 %	1.79 %
Moisture Content	3.0 Max.	0.0 - 0.3 %	0.21%
Loss on Ignition	6.0 Max.	0.7 - 2.6 %	0.91%
Sodium Oxide	-	0.1 - 0.7	0.14%
Potassium Oxide	-	0.5 - 2.2%	0.56%
Available Alkalis (as Na ₂ O)	1.5 % Max	0.5 - 0.8%	0.51%
Physical Test Results			
Fineness, retained on #325 sieve	34% Max.	8 - 16%	14%
Strength Activity Index			
Ratio to Control @ 7 days	-	81 - 95 %	94.8%

Ratio to Control @ 28 days	75% Min.	94 - 102%	99.5%
Water Requirement, % of Control	105% Max.	93 - 97%	94.2%
Soundness, Autoclave Expansion	0.8% Max.	-0.035 - 0.010	-0.033
Dry Shrinkage, Increase @ 28 Day	0.03% Max.	-0.01 - 0.010	-0.009
Density	-	2.35 - 2.45	2.36

Summary

The degree to which good quality fly ash will be compromised as the result of NOx or particulate emission systems in the future will depend upon technology choices made by utilities to reduce NOx, particulate matter emissions and plume opacity. However, STI's ammonia removal process can be utilized to remove the ammonia from contaminated ash, producing a high value material for use in concrete production. Recovered ammonia can be recycled to the generating unit for reutilization. This ammonia removal process can be installed as a stand alone system or can be used in conjunction with STI's successful fly ash carbon removal system.

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