Removing Ammonia from Fly Ash

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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. Specifically, mandated reductions in NOx , particulate, and SO_3 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.

The Problem in Concrete

The use of fly ash in concrete requires that the fly ash have specific physical and chemical properties [1]. The pozzolanic properties of the ash are activated in the concrete by 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:

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \leftrightarrow NH_{3(aq)} + H_2O$$

The dissolved molecular ammonia is easily released from solution as free ammonia gas. A strong odor of ammonia is unacceptable to the concrete producer, the contractor working with the concrete, and the ultimate concrete user.[2]

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.[3,4,5] Depending on the specifics of the location, including the amount of fresh air circulation, ammonia odor is not 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[6,7]

The cause of Ammonia in Fly Ash

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.[8] 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.[9] However, ammonia slip greater than 2 ppm may result in ash-ammonia contents of greater than 100 ppm, producing an unmarketable ash.[10] 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.[3,11] 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.

The STI Process

STI has patented a process that removes ammonia from fly ash.[12] 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[13]. 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 chemical reaction occurs rapidly once the compounds are dissolved.

The overall reaction can be generalized as:

$$(NH_4)_2SO_{4(s)} + CaO_{(s)} \rightarrow 2NH_{3(g)} + CaSO_4(s) + H_2O_{(g)}$$

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

$$CaO_s + H_2O \rightarrow Ca(OH)_{2(s)}$$

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

$$Ca(OH)_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2\ OH^-_{(aq)}$$

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.

$$Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow CaSO_4(s)$$

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

$$NH_4^+{}_{(aq)} + OH^-_{(aq)} \leftrightarrow NH_{3(aq)} + H_2O$$

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.[14]

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%). The pH of the resulting ash / lime / water mixture should be greater than pH 10.0. Very small quantities of alkali are added, depending on the natural pH of the ash. Typically, less than 1% $Ca(OH)_2$ is required. Calcium based alkalis are used which result in minimal alteration of the fly ash chemistry. No chemical residue is present which may interfere with other concrete ingredients. Extensive concrete testing has shown that the resulting ash performs as expected for a high quality pozzolan. The process is performed at ambient temperature.

In pilot plant trials conducted by STI, the continuous process has reduced the ammonia concentration of contaminated ash containing up to 1000 mg NH_3 / kg to less than 20 mg NH_3 / 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.

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