

Ammonia Removal from Fly Ash: Process Review

Headwaters Ammonia Slip Mitigation (ASM™) Technology

1010381

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Technical Update, December 2005

EPRI Project Manager

D. O'Connor

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ABSTRACT

For several years EPRI has examined topics related to ammoniated fly ash. Recently, there has been a focus of interest on ammonia removal processes, several of which are commercially available. For a more detailed investigation of these processes, it was determined that site visits to commercial operating facilities would be beneficial in understanding important aspects of the ammonia removal processes. This report focuses on the site visit and technology aspects of Headwaters' patented Ammonia Slip Mitigation (ASM™) technology.

Ammonia contamination of fly ash is considered problematic primarily due to the potential for adverse impacts associated with ash end-use as well as ash disposal. Most problems are related to personnel exposure, with gas-phase ammonia releases presenting a potential for both nuisance odors and in certain severe cases health impacts. Under the conditions of concrete manufacture, ammonia-contaminated ash is known to evolve considerable amounts of ammonia, varying with the conditions of concrete preparation and use. Dry land-filling operations may be impacted due to ammonia releases creating nuisance odor problems with operational personnel, and land-fill run-off may contain high levels of aqueous ammonia, potentially impacting water treatment or receiving waters. Wet disposal of ammoniated ash (ponding, etc.) may contribute to algae blooms in the receiving waters, and outflows to adjacent streams may have unacceptably high nitrogen levels. These issues have created the need for ammonia mitigation technologies, several of which have been developed.

The ASM™ process consists of treating ammonia-contaminated fly ash with chemical agents to destroy ammonia or reduce ammonia release. The chemical treatment reagent (principally calcium hypochlorite) is a strong oxidizer and can be added in a dry or liquid form to the ammonia-contaminated fly ash or can be used to treat various mixes/slurries containing fly ash. If added in the dry form, the reagent will be activated by the addition of water, subsequently reacting with dissolved ammonia in the ash or concrete slurry. For liquid applications of the treatment chemical, reaction with ammonia may take place immediately, but significant mixing must take place to fully disperse the liquid additive. The degree of ammonia reduction depends upon pH, temperature, time, initial dosage, and the presence of competing reducing agents.

The Headwaters ASM™ technology appears to be a convenient and effective technology. Although no independent analysis of treatment effectiveness was conducted as part of this study, the visited site appeared to be pleased with the results, and other industry data indicate that the process is effective at preventing ammonia evolution during various ash end-uses or disposal. The capital equipment requirement is rather small, making the process attractive on that basis. In addition, the system can be designed as an on-demand system, allowing for ash treatment only when necessary, thereby minimizing reagent costs. The visited site had two treatment options for fly ash, wet or dry, depending on the disposition of the final ash. This demonstrates the flexibility of the treatment system. Overall the general impression of the technology is highly favorable. The technology appears to be a low-capital, low-maintenance, cost effective approach for the treatment of ammoniated fly ash.

ACKNOWLEDGMENTS

The material presented in this report is largely due to the cooperation that was received relative to the site visit. We would like to offer our special thanks to the personnel of the host utility plant who were gracious in allowing a visit to their site and in offering valuable information. We would especially like to thank Dr. Rafic Minkara of Headwaters, Inc. who has assisted throughout the reporting process. His participation has been invaluable in developing this report.

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1

INTRODUCTION

For several years EPRI has examined topics related to ammoniated fly ash. Recently, there has been a focus of interest on ammonia removal processes, several of which are commercially available. For a more detailed investigation of these processes, it was determined that site visits to commercial operating facilities would be beneficial in understanding important aspects of the ammonia removal processes. This report focuses on the site visit and technology aspects of Headwaters Ammonia Slip Mitigation (ASM™) technology.

Ammonia Adsorption on Fly Ash

Ammonia adsorption on fly ash is a phenomenon that has been well documented in recent years in association with various ammonia-based environmental control technologies as applied to coal-fired boilers. The use of ammonia in the flue gas train for various purposes including SCR, SNCR, and flue gas conditioning for particulate control all result in the contamination of fly ash with various levels of ammonia. In general, the higher the level of ammonia exiting the control process, the higher the level of ammonia that will be found on the ash. However, a number of parameters will strongly influence the level of ammonia that ultimately would be present on the fly ash for any particular operating unit. These parameters include the time/temperature history of the flue gas, the control devices present in the flue gas train, the type of fuel being burned, and a number of fly ash-specific characteristics such as particle size distribution, bulk chemical composition, and surface chemistry. In addition, flue gas components such as SO₃ will greatly affect ammonia adsorption. This is especially important since SO₃ is sometimes injected into the flue gas to aid in particulate control, and because SCR catalysts promote the formation of SO₃. It is not uncommon for both ammonia and SO₃ to be injected into flue gas as conditioning agents to improve particulate capture in electrostatic precipitators, creating a favorable scenario for ammonia deposition on the fly ash. It is known that eastern bituminous coals produce acidic ashes having a high affinity for ammonia, especially since the presence of moderate to high levels of SO₃ associated with the combustion of these fuels promotes ammonia adsorption. The adsorption level of ammonia for eastern bituminous ashes is on the order of 80% (as a rule of thumb) for ammonia slip levels below 5 ppmv. This translates to approximately 100 ppmw of ammonia on the fly ash for each 2 ppm of ammonia slip leaving the control process (assuming a coal with 10% ash). The percentage of ammonia captured by the fly ash may be reduced at high levels of ammonia slip due to the saturation of the fly ash, although the fly ash is capable of supporting high levels of ammonia, ranging in the thousands of ppm for ash fines. Other fly ashes, such as those from Powder River Basin coals, where both the SO₃ level is low and the ash pH is high (basic), will exhibit much less ammonia adsorption, such that facilities burning these types of coals may rarely see problematic levels of ammonia on the associated fly ash.

Ammonia Chemistry

In most cases, ammonia is present on the fly ash surface as a mixture of ammonium sulfate (AS) and ammonium bisulfate (ABS). Other ammonia compounds may be present, or ammonia may

be physically adsorbed on the fly ash surface, but ammonia-sulfur compounds are principally present when flue gases contain even relatively low amounts of sulfur dioxide (500 ppm or greater). Due to this finding, it is believed that the presence of SO₃ in the flue gas represents a major driving force for ammonia adsorption/deposition. Both AS and ABS form at relatively high temperatures and typically will begin forming at some point in the unit's air preheater. The deposition of these compounds on fly ash surfaces, equipment, and ductwork occurs quite rapidly, and this deposition is often the primary source of air preheater fouling associated with ammonia-based controls. In general, the adsorption/deposition process is reversible to a large degree.

Ammonia compounds are strongly affected by pH. In terms of gas/liquid equilibrium, ammonia is highly soluble in water at pH levels below 7. However, when pH is raised, ammonia will evolve into the gas phase. This phenomenon is the source of much of the behavior noted with ammoniated fly ash. For instance, acidic ashes, even when wetted, tend not to evolve appreciable amounts of ammonia as long as the pH remains low (acidic). However, when caustic materials are added in sufficient quantities to raise the pH above 7 (such as with the addition of lime in concrete manufacture) the ammonia may be rapidly released. Ammonia is often highly leachable from acidic ashes, such as in sluicing or land-filling operations, producing aqueous streams with high ammonia contamination. Subsequent pH change in these aqueous streams may result in the gas-phase evolution of ammonia.

Adverse Impacts of Ammonia Contamination

The adverse impacts of ammonia contamination of fly ash are mainly related to environmental impacts and health and safety concerns. Most contaminated ashes having ammonia levels consistent with common environmental control process conditions have not been found to adversely affect the physical or chemical behavior of the ash during ash end-use, such as during the manufacture of concrete. However, because even relatively low levels of ammonia can produce nuisance (odor) and health problems and have adverse environmental impacts, ammonia contamination of fly ash is extremely important to the industry. It has the potential to disrupt both ash sales and ash disposal activities. Some of the potential adverse consequences of ammonia contamination are outlined below.

- Gas-phase evolution during handling and transport, causing odor problems for personnel.
- Long-term gas-phase evolution after land-filling causing chronic personnel exposure issues, mainly due to odor.
- Highly contaminated run-off water from sluicing, ponding, and land-filling causing environmental damage to receiving waters.
- Acute ammonia evolution during end-use activities such as concrete manufacture, causing odor problems for personnel, and potentially health problems in enclosed areas.
- Chronic ammonia evolution during end-use, creating nuisance odor problems with concrete pours, etc.

Ammonia Removal Processes

A number of ammonia removal processes are commercially offered. These processes can be divided into two general types, thermal and chemical, although the designations are not always clear-cut, since some removal processes will rely on both chemical and physical processes. The Headwaters Ammonia Slip Mitigation technology is considered a chemical process.

Thermal Removal Processes

Thermal removal processes rely on heat to dissociate ammonia compounds or to force physically adsorbed ammonia from the fly ash surface. In either event the result is to volatilize the ammonia from the solid ash phase to the gas phase where it can be swept away, or thermally decomposed. In lower temperature applications, ammonia will be liberated from the fly ash surface creating an ammonia-laden gas stream. This evolved ammonia may then be treated to destroy the ammonia prior to environmental release. In some high-temperature applications, the thermal energy may be sufficient to thermally destroy the ammonia molecule, such that ammonia removal and subsequent destruction is integral to the process. In essence, thermal removal processes reverse the ammonia deposition/adsorption process. The process is both time and temperature dependent, and chemical agents may be used to enhance the process performance. Thermal processes require considerable thermal energy and fly ash handling, but are very efficient in removing ammonia and generally have no detrimental effect on other fly ash characteristics. In some cases fly ash characteristics for end-use are improved in addition to the removal of ammonia by decreasing moisture or carbon content.

Chemical Removal Processes

Chemical removal processes rely on certain chemicals to either destroy ammonia, combine with ammonia to limit its potential for volatilization, or force its release from the fly ash surface where the off-gas can be subsequently treated. Some treatments may also cause a reaction with the ammonia to form other, more benign, compounds. Chemical removal processes typically require less capital than thermal removal processes, but may have a higher variable operating cost due to the cost of the chemical itself. The added chemical may have the potential to affect ash properties, but most treatments are designed to avoid any adverse impact on the final use or disposal of the fly ash. In general, chemical removal processes are less well demonstrated at full scale than thermal removal processes, but economic incentives for their development are strong, and they are becoming more widespread.

Headwaters ASM™ Process Background

Headwaters has developed an ammonia removal technology for fly ash, which consists of treating ammoniated fly ash with chemical agents to destroy ammonia or reduce ammonia release. The chemical treatment reagents (various hypochlorites – most frequently calcium hypochlorite) are strong oxidizers and can be added in a dry or liquid form to the ammonia-laden fly ash and used to treat various mixes/slurries containing fly ash. In the dry form, the reagent, activated by the addition of water, reacts with dissolved ammonia in the ash or concrete slurry. If added in a liquid form, the reaction may be more immediate, but sufficient mixing to fully disperse the chemical would be required. Ash conditioning for disposal, such as with pug-milling, would represent a favorable scenario for liquid treatment.

The rate of ammonia reduction depends upon pH, temperature, time, initial dosage, and the presence of competing reducing agents. The reaction of ammonia and hypochlorite in water is complete within a few minutes. Theoretically, a 1:1 molar ratio of hypochlorite to ammonia (Cl:N) produces monochloramine. An increase in the dosage results in the formation of nitrogen compounds with higher oxidation states (e.g., N₂ and NO₃⁻). Theoretically, a stoichiometric molar ratio of 1.5:1 (as shown below) is sufficient to convert ammonia to nitrogen gas. Higher dosages might be required to compensate for elevated carbon contents or less than optimal pH. A further increase in dosage (over 2:1 molar ratio) could result in the formation of nitrates and chloride salts.

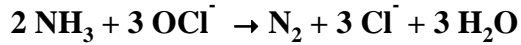


Table 1-1 gives some removal comparisons, made publicly available by Headwaters, for various reagent dosages for an unidentified ash source with an initial level of ammonia of 600 ppm.¹ Note that in these tests, the reagent was pre-dissolved in water and sprayed on the ash, followed by mixing. A generalized process flow diagram is depicted Figure 1-1, showing the addition and mixing of the chemical additive prior to truck transport from the generating site. In this depiction, the chemical is added dry, although it is possible to add the chemical as an aqueous solution as previously discussed.

Table 1-1
Ammonia Removal Data¹

Reagent Dosage (Cl:N)	Required Chemical ^a Addition (lb`s/ton)	Ash Moisture (%)	Ammonia Evolution as Determined by Headwaters (ppm)	Ammonia Reduction as Determined by Headwaters (%)
0.0:1.0	0	0%	500	0%
0.5:1.0	4	1%	300	40%
1.0:1.0	8	2%	30	94%
1.5:1.0	12	3%	20	96%
2.0:1.0	16	4%	15	97%

^afor ash w/600 ppm ammonia

¹ Data are based on publicly available commercial information disseminated by Headwaters. No independent assessment by EPRI as to the accuracy of the claims has been made.

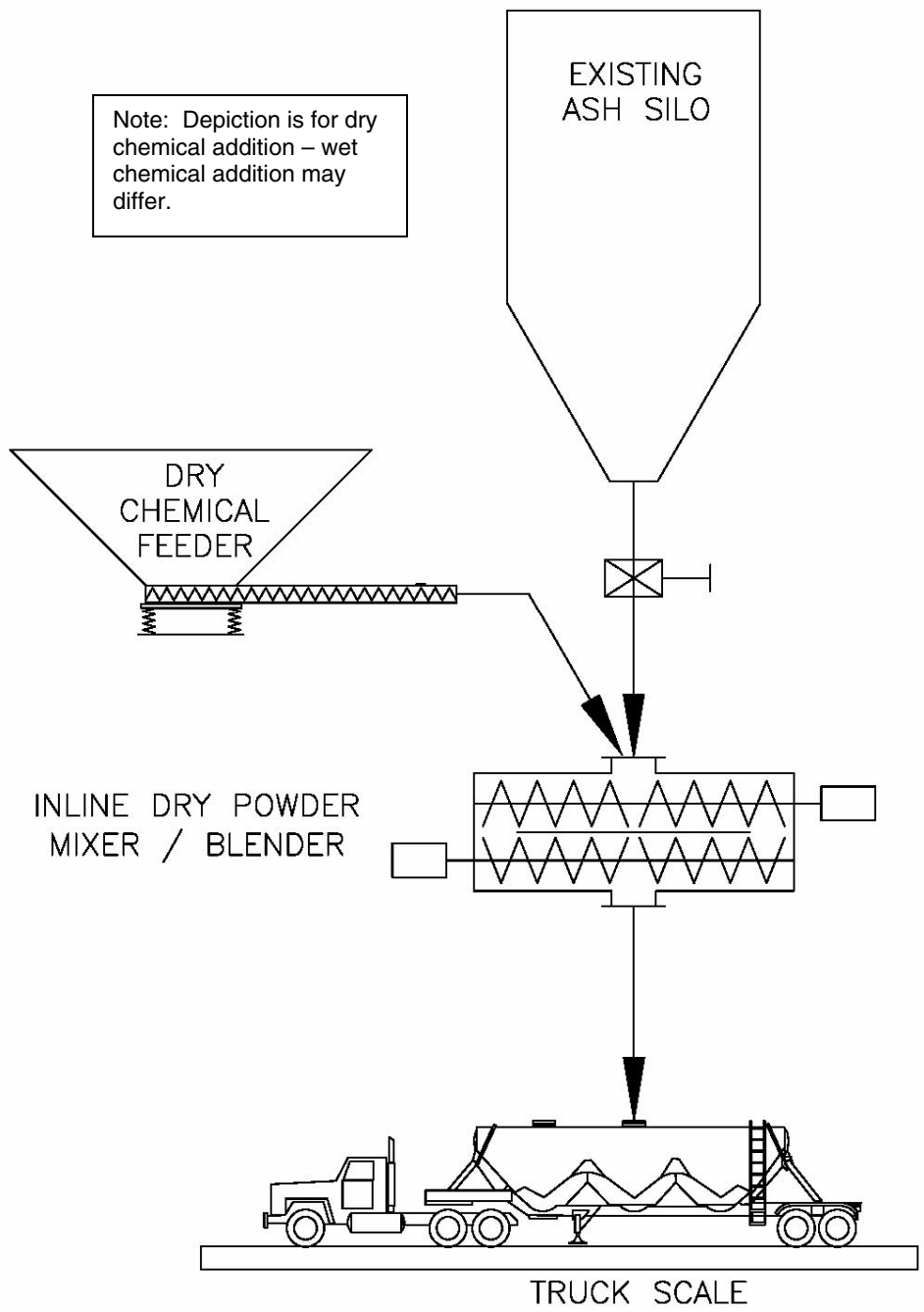


Figure 1-1
Early Conceptual Process Flow Diagram

The Headwaters process has been commercialized at full scale, with the first installation processing approximately 150 tons per hour of ash and completed with less than \$500,000 capital. Typical industrial systems would be designed in two sizes, roughly 150 tons per hour and 300 tons per hour. Depending on space and headroom availability, most dry-feed systems could be installed at the existing silo, or within existing buildings for truck loading, etc. Installation times will vary according to the specific site, with a 6-9 month total installation time (including equipment lead-time) being typically required. Specialized equipment procurement and delivery represents the bulk of the installation lead time.

2

SITE VISIT

Site Background

The visited full scale operational site for the ASM™ technology was located at a utility plant in the northeast U.S. The plant fires eastern bituminous coal and is equipped with several operating units capable of a total electrical output of approximately 200 MW. The ASM™ system is designed to treat the entire fly ash output from the plant, if required. The reagent used is calcium hypochlorite. Ash is hauled by truck and loaded in an enclosed loading bay, over which the ash hoppers and ASM™ system are located. Figure 2-1 shows a photo of this enclosed ash loading bay.



Figure 2-1
Truck Loading Bay for Fly Ash

The plant is equipped with SNCR technology for the removal of NO_x, and thus has relatively high levels of ammonia slip compared to an SCR installation. The requirement for an ammonia removal technology installation was recognized prior to the installation of the SNCR and thus the installation of the ASM™ technology was installed essentially as a preventative measure, rather than as a response to any experienced problems associated with ammoniated ash. Typical ash contamination levels of ammonia are on the order of 75 to 250 ppmw, depending on the source of the ash. The historical maximum treated ammonia has been approximately 300 ppmw.

Initially, measurements of ammonia contamination were made rather frequently to insure that accurate data was being used for the determination of the required treatment level of calcium hypochlorite for the ash. However, data has shown that the ammonia contamination level is relatively steady and ammonia measurements are taken on a daily basis. During operational changes (SNCRs in and out of service, changes in unit load, etc.) the ammonia level of the ash may be measured more frequently. The calcium hypochlorite treatment level can theoretically be adjusted as often as desired, but at this facility, treatment level is typically adjusted only daily, if required. The system is designed to treat at a dosage rate of 0-6 pounds of calcium hypochlorite per ton of fly ash, with the typical dosage rate being approximately 2-3 lb/ton.

A number of potential end-uses for the fly ash from the plant are possible. These include use in cement/concrete manufacture and flowable fill. Alternately, the ash may be land-filled. No long-term ash sales contracts are in place, and thus the disposition of the fly ash may change from day to day. For this reason the ASM™ technology has been designed as an “on-demand” system allowing operators to make the decision whether to treat the ash according to its final disposition. This can be done on a truck-by-truck basis if needed. Ash can be loaded dry, or can be pug-milled using water for dusting control (typically for hauling in open trucks for disposal). This “wet” option is typically used to treat high-carbon ash generated at the plant. The ASM™ technology has been designed to treat the ash slightly differently depending on whether it will be hauled dry, or wet after pug-milling. This will be discussed in more detail below.

Process Design

The specific design of the ASM™ technology is dictated by the needs of the particular facility on which it is installed. At the visited facility, as mentioned, the system was designed as an on-demand system, giving the operators full control of whether to treat the ash on an as-needed basis. Further, as mentioned previously, the ash can be treated using dry calcium hypochlorite when dry-hauling of the ash is required for use in cement, for example, or using aqueous slurry of calcium hypochlorite in the case of pug-milling prior to disposal where water is used to generate a dampened ash preventing dusting. These two scenarios will be discussed separately, below. In either case, the treatment of the ash requires that the relative flow rates of both calcium hypochlorite and fly ash be known.

Dry Ash Treatment

When ash is treated dry, the metered calcium hypochlorite is simply mixed with the fly ash as the material is loaded onto the truck. Thus, this on-demand system treats the fly ash just prior to truck loading. Upon mixing with water, such as with concrete manufacture, the actual chemical reactions take place which result in the destruction of ammonia and prevent its evolution. Figure 2-2 shows the schematic for the dry fly ash treatment option. Following the general flow of calcium hypochlorite, the material is transferred from drums located at ground-level to the day hopper bin. From this bin, the material is conveyed to a small hopper just above a vibratory feeder where the rate of calcium hypochlorite is metered (discussed in more detail below). The chemical then combines with ash at the coriolis-type mass flow meter (where thorough mixing occurs), which receives fly ash from the fly ash silo located above. The treated fly ash is then discharged into a waiting truck.

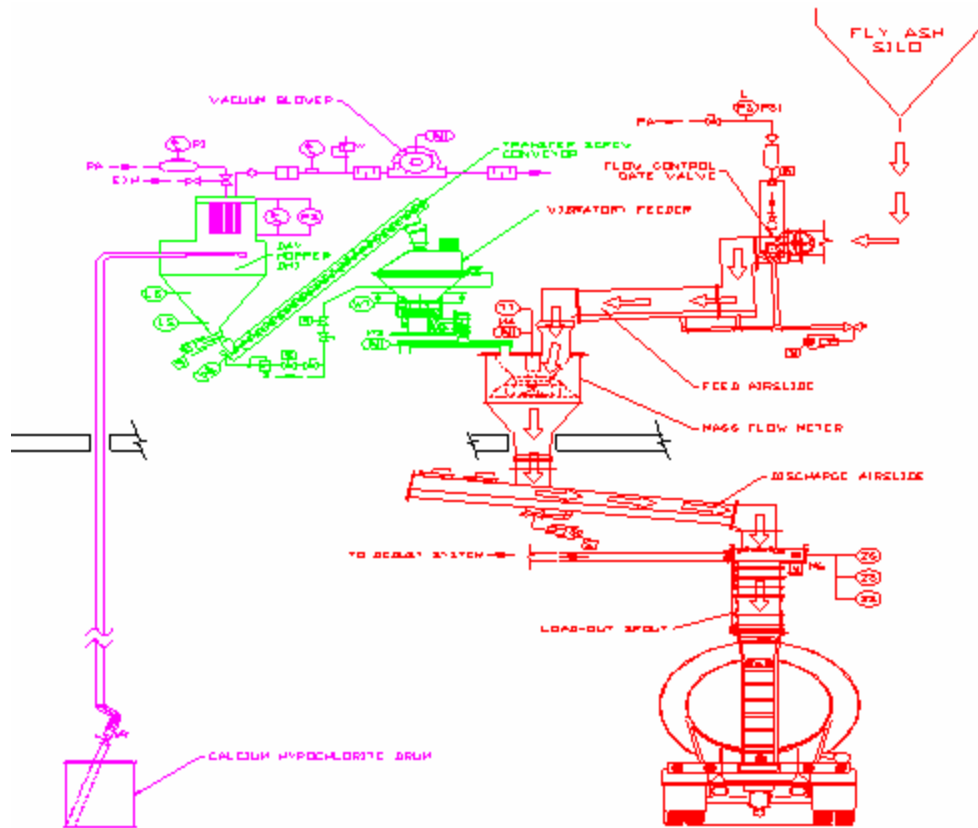


Figure 2-2
Flow Diagram – Dry Fly Ash Treatment

Wet Ash Treatment

In the event that ash is to be pug-milled, a slightly different process scenario is used as compared to dry treatment. This is termed “wet ash treatment”. In this scenario, the appropriate amount of calcium hypochlorite is added to water, prior to combining with the ash in a pug-mill. The fly ash flow rate for the wet treatment option is not directly measured due to the consistent flow rate of fly ash in this operating mode (see additional information under “Fly Ash Flow Measurement,” below). The calcium hypochlorite and water are blended in a conical chamber to create a low-solids slurry/solution which is combined with the fly ash in a pug-mill, just prior to truck loading. Figure 2-3 shows the process flow diagram for this scenario. Figure 2-4 shows the conical mixing chamber where the calcium hypochlorite slurry is created. This chamber is situated just below the day bin where calcium hypochlorite metering occurs.

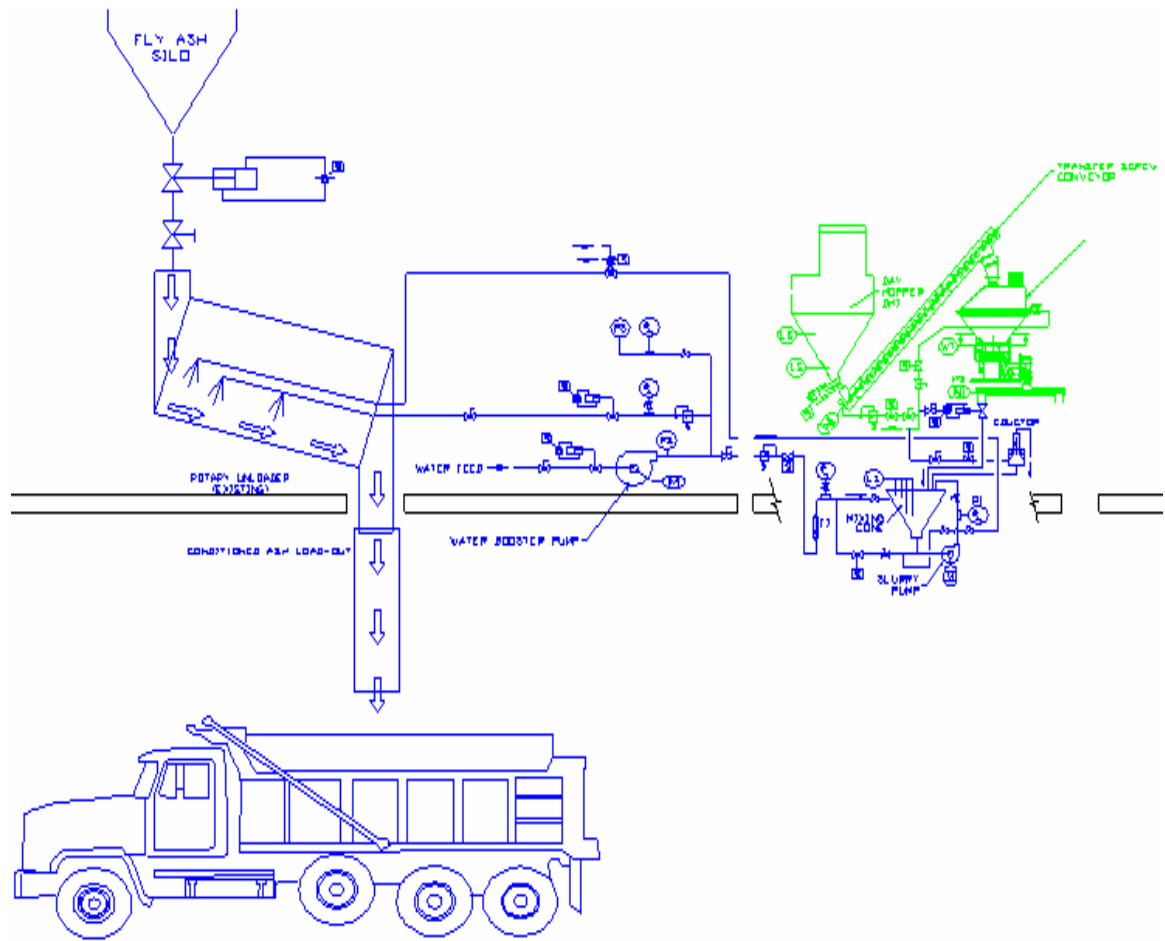


Figure 2-3
Flow Diagram – Wet Fly Ash Treatment Option

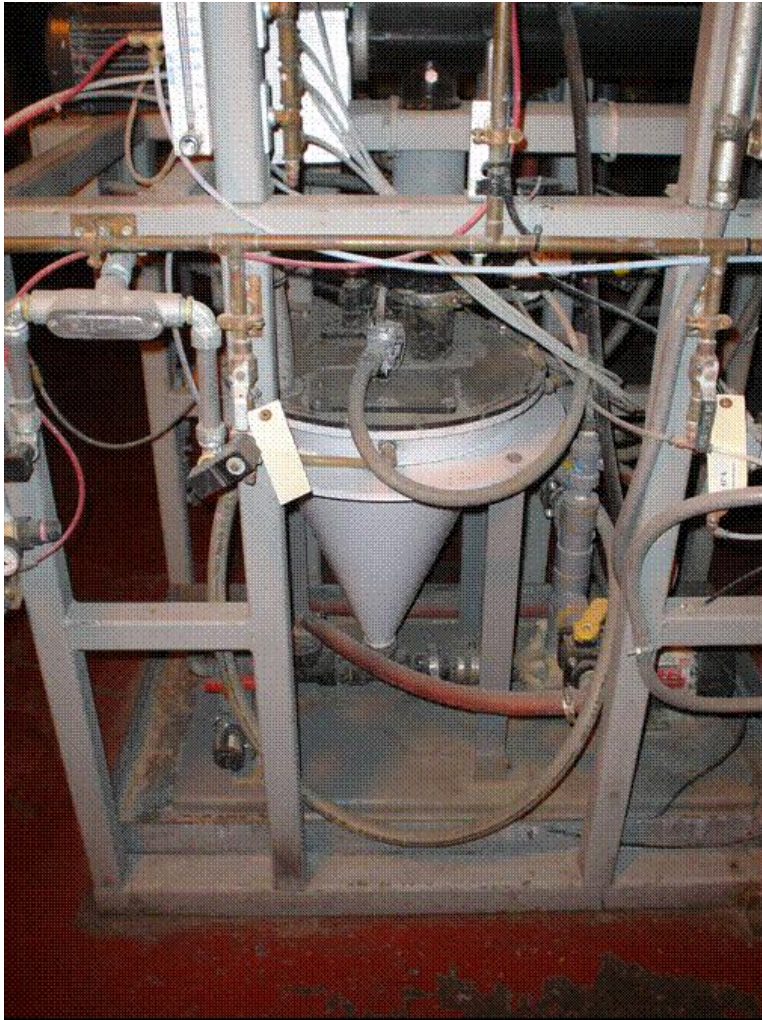


Figure 2-4
The Conical Calcium Hypochlorite/Water Mixing Chamber

Equipment Design

The primary equipment for the ASM™ technology is housed on a floor elevation above the truck loading bay. Thus, the ash is treated just prior to entering the truck. The diagram in Figure 2-5 gives a perspective as to the size of the physical equipment with respect to an ash hauling truck. The system is generally quite space efficient. Figure 2-6 shows a photograph which encompasses the majority of the necessary equipment for the system. Not shown is the calcium hypochlorite day bin and the coriolis metering device for ash flow (both discussed subsequently).

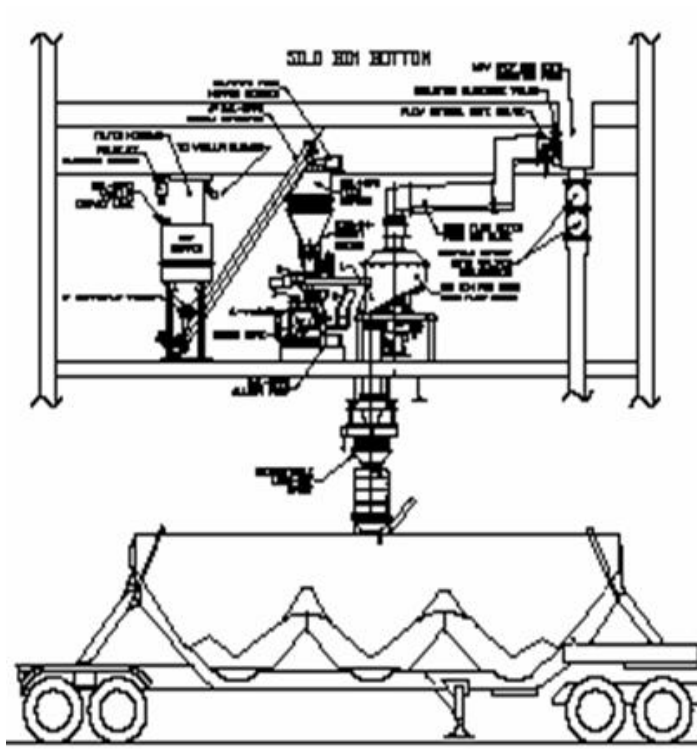


Figure 2-5
Diagram Showing Relative Size of Installed Equipment

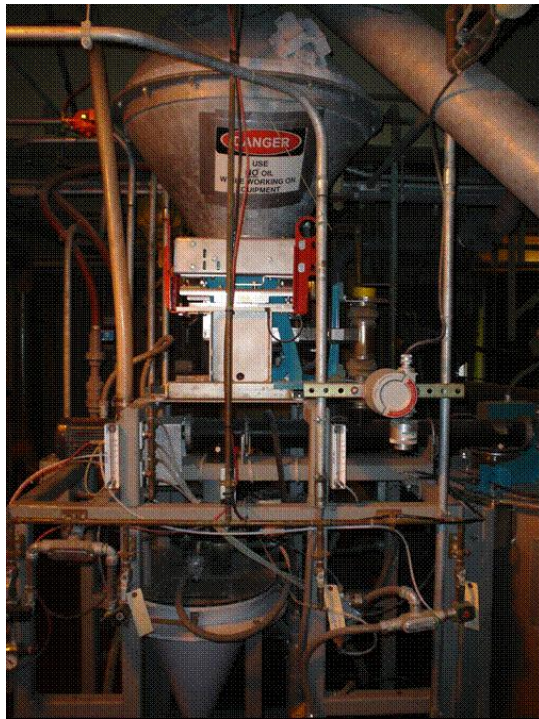


Figure 2-6
Process Equipment—Calcium Hypochlorite bin with load cells, above, water and calcium hypochlorite mixing device, below

The calcium hypochlorite is stored in various bins as part of the equipment design. A day bin is located near the point of metering and mixing the calcium hypochlorite. This day bin is filled from drums located at ground level and can hold approximately 3-5 drums of calcium hypochlorite. (See more on chemical storage and transfer under “Material Handling”). Figure 27 shows this day bin. The transfer duct shown in the lower right corner of this photo feeds into the small calcium hypochlorite bin where weighing and metering occurs (see upper part of photo – Figure 2-8).



Figure 2-7
Calcium Hypochlorite Day Storage Bin

Calcium Hypochlorite Flow Measurement

As previously mentioned, the treatment rate of calcium hypochlorite is typically 2-3 pounds per ton of fly ash treated, for the site visited. Thus, a very small amount of calcium hypochlorite is required relative to the fly ash, on the order of only 0.1%. From chemical storage drums, the calcium hypochlorite is loaded into the day bin. This day bin contains sufficient material to treat the fly ash produced in a day. From this day bin, calcium hypochlorite is transferred to the small hopper above a vibratory pan. The vibratory pan is used to control calcium hypochlorite flow, with weight differential being utilized to actually determine the mass flow rate. Sufficient material is transferred to this hopper to treat at least one truck, based upon the maximum design dosage rate, to prevent interruption for refilling. Since weight differential is the primary mass flow measurement, this hopper can not be filled continuously. The small load cell-equipped hopper above the vibratory feeder is depicted in Figure 2-8. This photo represents an angle 90° to that shown in Figure 2-6, with generally the same equipment being shown.

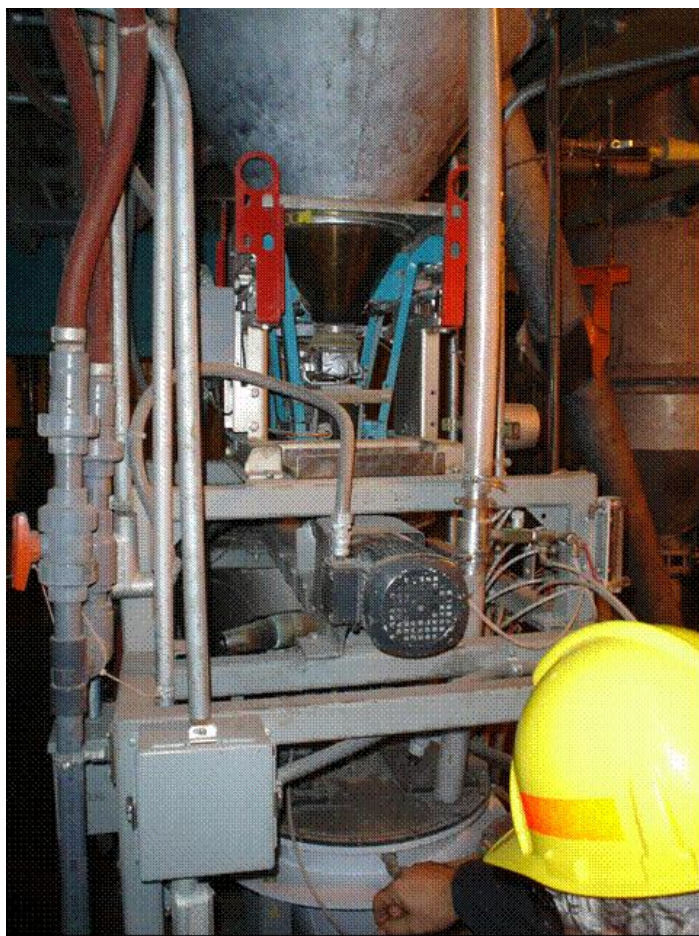


Figure 2-8
Hopper Containing Calcium Hypochlorite Mounted on Load Cell

Fly Ash Flow Measurement

Fly ash flow rate is measured utilizing a coriolis-type flow measuring device. The device works by spinning fly ash radially outward from a rotating bladed disk. The torque created by this action is directly proportional to the mass flow rate of the solid material being metered. These systems work very well for free flowing fine solid materials such as fly ash. The coriolis device is shown in Figure 2-9 (see arrow), with the ash transfer duct shown above. The coriolis meter operates in conjunction with a modulating flow control valve to maintain a steady flow of fly ash. The flow of calcium hypochlorite is then determined from the fly ash flow rate as a function of the desired dosage rate. During wet ash treatment, the fly ash flow rate is not measured using the coriolis metering device. This is due to the very consistent flow rate of ash to the pug-mill and the less stringent treatment requirements for the pug-milled ash, which alleviates the need for continuous ash flow measurement. A flow measurement device could be easily installed for the wet treatment option if desired.

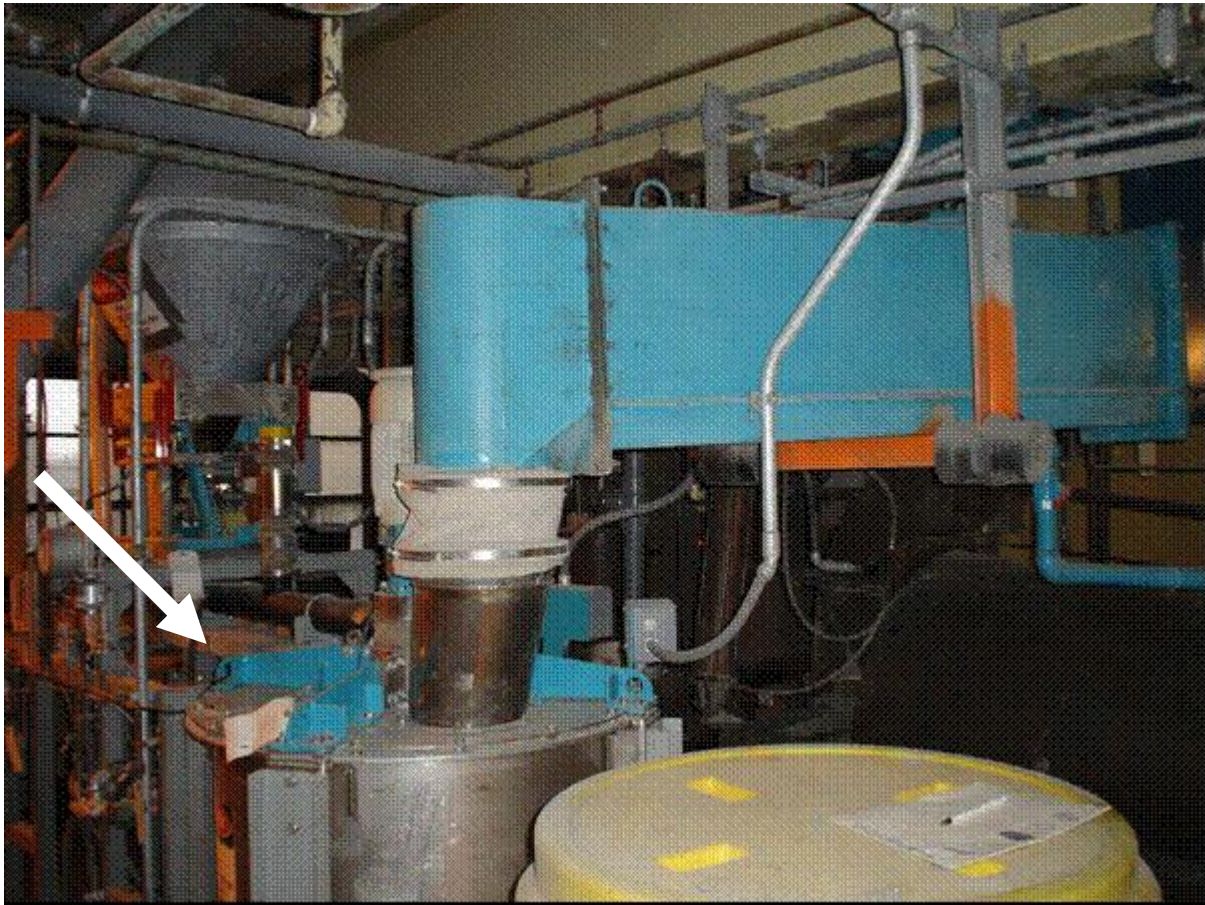


Figure 2-9
Coriolis-Type Flow Measuring Device and Ash Transfer Duct

Process Control

The system has a relatively straight-forward process control loop. The primary input to the control loop is the fly ash flow rate and treatment level (which is a manual setting based upon the approximate level of ammonia in the ash and the required ammonia reduction). The system computes the required flow rate of calcium hypochlorite and adds this either directly to the ash or to the water prior to mixing with ash in the case of the pug-milling scenario. Again, this metering of calcium hypochlorite is done on-demand as individual trucks are being filled. The primary control system electronics are located on a panel near the process equipment. Figure 2-10 shows the primary control panel for the system (with cabinet door opened to left).



Figure 2-10
Primary Control Panel

Material Handling

Calcium hypochlorite is stored in various bins and containers as part of the process. Generally, the storage locations are in close proximity to one another, minimizing long material transfers. The calcium hypochlorite is delivered to the site in chemical drums. These drums are stored at ground-level in the truck loading bay. From these drums, it is transferred pneumatically to the day bin. From the day bin, the calcium hypochlorite is transferred mechanically to the small hopper above the vibratory feeder. This is done on an automatic basis, based on the amount of

calcium hypochlorite available in this hopper. None of the material transfers are performed simultaneously. The relatively small amount of calcium hypochlorite required makes the designed material handling operations convenient and efficient.

3

ECONOMICS

Overall, the relatively limited equipment required and the small amounts of treatment reagent needed make the ASM™ technology attractive from a capital perspective. An on-demand system helps to minimize reagent usage, preventing ash from being unnecessarily treated when not required. Since the technology is installed in conjunction with other plant equipment associated with ash loading, etc., the capital costs are highly site specific. Systems designed to treat both dry and wet ash, with common controls, would typically cost between \$500,000 and \$1 million. Operating costs would include the chemical costs and other O&M costs. Contractually, arrangements are flexible and depend on the ash marketing and management scenarios. Headwaters told the author that it considers various scenarios for the installation of the process, including technology licensing, turnkey installation, and comprehensive ash service agreements with equipment financing.

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CONCLUSIONS

The Headwaters ASM™ technology for the treatment of ammoniated fly ash appears to be a convenient and effective technology. Although no independent analysis of treatment effectiveness was conducted as part of this study, the visited site was pleased with the results, and unpublished industry studies indicate that the process is effective at preventing ammonia evolution during various ash end-uses or disposal. Vendor data show that high removal efficiencies are possible (>95%), but in most cases the required removal efficiency may be substantially less. The capital equipment requirement is rather small, making the process attractive on that basis. In addition, the system can be designed as an on-demand system, allowing for ash treatment only when necessary, thereby minimizing reagent costs. The site visited had two treatment options: one for dry fly ash, and one for wet fly ash, depending on the final disposition of the ash. This demonstrates the flexibility of the treatment system. The technology design allows for varying treatment levels to compensate for both the level of ammonia in the fly ash as well as the desired level of ammonia removal, which can be set according to fly ash end-use. The control of the system is straightforward, with the primary input from the operator being the chemical addition dosage rate. Overall the general impression of the technology is highly favorable. The technology appears to be a low-capital, low-maintenance cost effective approach for the treatment of ammoniated fly ash.

Export Control Restrictions


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