Abstract

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Ammonia in PFA and cementitious products manufacture

In order to reduce NO_x emissions, increase precipitator efficiency from coal fired power stations and to ensure compliance with the EU Large Combustion Plant Directive, ammonia (NH_3) will need to be injected in the furnace gases of many UK coal fired power stations. While ammonia does not have any detrimental effects on the performance of concrete, concerns have been expressed about the Health & Safety aspects of possible contamination of Pulverised Fuel Ash (PFA)/fly ash[a].

Ammonia injection is used to convert NO_x gases to nitrogen when the furnaces gases pass over Selective Catalytic Reduction (SCR) units. Ammonia may also be injected into the furnace gases to enhance the efficiency of electrostatic precipitators by increasing the ionising potential. Excess ammonia not converted within the SCR may thereby be found within the PFA. This ammonia will be released when used in concrete and aircrete block manufacture, due to the high pH of these products. However, this raises a number of issues such as the measurement of ammonia in PFA. With there being no recognised test method and the existence of a considerable number of techniques, what is an acceptable level of ammonia contamination and what are the possible short and long term effects on these products?

This paper will review the issues associated with the use of ammonium injection, measurement of ammonia in PFA, the possible effects on concrete and aircrete block properties, experience from mainland Europe and its use in the UK. In addition it will look at the techniques for post processing PFA to remove ammonia.

{a} PFA is the most common term for coal fired power station ash in the UK, whereas many other countries refer to this as fly ash.

Introduction

The ever demanding environmental legislation within the EU requires that coal fired power stations reduce further their emissions to levels previously thought impractical. Nitric and nitrogen oxides (NO_x) have been seen as being a particular problem being associated with acid rain, smog and human health issues. Though low NO_x burners have been fitted to all UK coal fired power stations over the last 10 years, EU regulations such as the Large Combustion Plant Directive (LCPD)[1] require further reductions in emissions, or the power stations will be forced to close down. These limits will only be achieved by the fitting of gas treatment units, such as selective catalytic reduction.

Selective Catalytic Reduction (SCR)

These low levels of NO_x emissions can only be achieved by the injection of ammonia into the furnace gas stream, which is then passed over a SCR unit. This converts any NO_x to ammonium compounds, oxygen and nitrogen. One additional beneficial effect of ammonia in the furnace gas stream is it aids the ionisation of the PFA particles within the electrostatic precipitators, thus improving their efficiency in removing the ash from the gas stream. This is generally used where low sulphur coals are routinely being burned, such as anthracite.

The formulas for the chemical conversion within the SCR are as follows:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \quad \text{and} \quad 6NO_2 + 8NH_3 = 7N_2 + 12H_2O$$
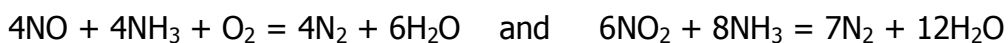
There are many places the SCR unit can be placed in the gas stream, between the furnace and the precips (high dust) being the most common, though after the precipitators (low dust/tail end) and even after FGD equipment (low temperature). As the SCR's work only at higher temperatures, 320 – 400°C, the low dust and low temperature positions require the gases to be re-heated, hence why they are least common. In theory the above reactions don't need a catalyst but the natural reaction rate makes SCR necessary in order to prevent high levels of ammonia being required.

Ammonium injection does have some drawbacks, in that it may not be fully converted to stable compounds within the SCR for one or more of the following reasons;

- if the levels of injected ammonia are higher than is necessary to convert the NO_x being produced into nitrogen and oxygen within the SCR, or;
- the gas temperatures passing over the SCR are too low reducing conversion efficiency, or;
- SCR efficiency is somehow impaired, e.g. gas flow issues, SCR needs cleaning or replacing, arsenic poisoning, calcium sulfate masking, etc[2].

The result is the excess ammonia is deposited on the fly ash particles as various ammonium salts, so called ammonia slip. This can also have detrimental effects elsewhere within the boiler, such as the formation of ammonium compounds on the various surfaces and lead to an ammonium chloride plume being emitted from the stack.

The efficiency of SCR is sensitive to load factor, for example a lower gas stream velocity leads to greater contact time with the SCR and more efficient removal. The ammonia input is controlled by monitoring the NO_x output. Urea can be used as an alternative to ammonia, which works exactly the same. Ammonia on demand plants are being used in some power stations.

The catalyst in an SCR will last ~2 to 3 years and to ensure efficiency, the gas streams must be flow modelled to prevent erosion problems and ensure efficient working of the system. They should be tuned to ensure the ammonia concentration is consistent across the whole area of the catalyst and cleaning devices may be used on the catalyst in order to reduce ammonia slip. Another issue with SCR is that SO_2 is turned into SO_3 in the catalyst (it doubles the output approximately) which can lead to a sulphuric acid plume, e.g. a brown tinge to the station exhaust plume, with enamel plates being used in colder parts of the furnace to prevent acid corrosion. Ammonia slip also affects the air heater efficiency. Ideally the plates should be cleaned twice a year using 400bar pressure – but this takes 1 week to do! Hence controlling ammonia slip to <2ppm (~equivalent <100ppm in the fly ash) is important not only for the fly ash but to maintain air heater efficiency.

An alternative is selective non-catalytic reduction (SNCR) which is less complex and less expensive but also less efficient than SCR. Again ammonia is injected into the furnace to convert NO_x to N, but it requires sufficient reaction time in the furnace, through mixing and a temperature of 760 to 1,093°C to be effective. As a result higher levels of NO_x and a greater risk of ammonia slip are to be expected.

Where ammonia is simply being used to improve precipitator efficiency, the injection levels can be considerably higher than would be used for SCR purposes rendering the ash useless in many applications unless treated in some manner.

It is believed that up to 80% of ammonia slip is adsorbed on the fly ash with the majority of the ammonia existing as ammonia salts, ammonium sulfate and bisulfate. In addition some ammonia will be chemically absorbed onto the residual carbon surfaces. There is a degree of ash particle size dependency and there is more ammonia slip found in finer ash particles.

The adsorption capacity of fly ash has been found to be a minimum of 350mg/kg (NH_3) at 350°C, i.e. at about the operating temperature of an SCR unit. At lower temperatures (<120°C) moisture will increase the adsorption of ammonia further. However, the

adsorption capacities of fly ash differ with coal source and firing conditions and the differences are not clearly understood.

Immediately ammoniated fly ash is mixed with water and a strong alkali medium, such as in concrete or aircrete block manufacture, the ammonia is released as a gas. It is this reaction that the commercially available ammonia removal units rely on. If the ash is simply mixed with water only, then the gaseous ammonia may be released very slowly, depending on the inherent chemistry/alkalinity of the fly ash. With high concentrations in the fly ash detectable levels of ammonia may be released over a period of days [3]. The rate of emission will reduce relatively quickly. The ammonia released is directly proportional to the ammonia content of the fly ash and the quantity of fly ash and/or fly ash based aggregates being used.

Gaseous ammonia is not pleasant and at high concentrations can cause health problems, however, there is no evidence it causes any significant deleterious effect on cementitious based products, e.g. blocks and concrete – it is primarily a Health and Safety issue.

Health and Safety Issues

Ammonia is a colourless alkaline gas which is readily soluble in water. Its solubility in water can cauterise respiratory tracts resulting in death at concentrations of 5,000ppm by volume (ppmv). It is an inhalation hazard but NOT a skin absorption hazard, though it begins to affect skin moisture at 10,000 ppmv, at significantly higher levels than at which respiratory failure will occur. The exposure limits[4] for TWA (Time Weighted Average) exposure is 25ppmv (18mg/m^3), STEL (Short Term Exposure Limit) of 35ppmv (25mg/m3) and IDLH (Immediate Danger to Life & Health) of 300ppmv. At concentrations of around 50ppmv and above, ammonia will cause irritation to the eyes and respiratory tract. Of course ammonia is the basis for smelling salts, used to revive the semi-conscious, but the exposures are relatively small, with the Odour Detection limit for humans being about 3ppmv. In relation to other odorous gasses, the human nose is particularly sensitive to ammonia.

Measurement of Ammonia in fly ash

As ammonia has potential to causes health problems and is a pungent material, the measurement of the ammonia content of fly ash would seem to be an important and critical test to carry out. It was therefore with some surprise when researching this area that numerous different methods of measuring ammonia exist, with varying repeatability of which no standardised method has ever been established as such.

There are many ways to detect ammonia. High concentrations are easy to detect because the gas has a very penetrating odour. To quantify the ammonia concentration or determine lower concentrations of ammonia, the human nose fails. However, on

many occasions, the ammonia concentration has to be known, even at ultra-low concentrations of less than parts per billion in air by volume (ppbv).

Test methods

There are numerous methods of testing ammonia, ranging from direct wet chemistry through to Radar and Infra-Red Spectrometry. It is difficult to resolve which of these methods are best suited for use in the fly ash industry and which ones are sufficiently accurate as manufacturers claims seem to vary wildly. Rathbone & Majors[5] reviewed various techniques for fly ash, mortar and concrete in 2003. Since then more potential methods have appeared as technology becomes ever more advanced. The following section attempts to summarise the various techniques that could be employed.

Measurement of Ammonia Gas

These methods are suitable for ambient monitoring of NH_3 gas, e.g. for health and safety monitoring. Alternatively, they could be used for measuring ammonia in ash, for example by heating or mixing the ash in alkaline solution and testing the gases evolved.

Optical Absorption Spectroscopy: Optical absorption spectroscopy is used in the most sensitive and selective ammonia detectors when looking for ambient ammonia. Systems with a detection limit of 1 ppb, that do a full measurement in 1 second, have been reported. Such systems basically use a laser and a spectrograph. They are very expensive and attempts at miniaturisation result in reduced sensitivity. They may use visible, ultra violet or infrared light to carry out the analysis, with infrared seeming to be the preferred.

Fourier transform infrared spectroscopy (FTIR) is a type of spectroscopy where all the light passing through the gas is analysed by creating interference patterns which are analysed mathematically using a computer and the Fourier Transform. This is opposed to only analysing the wavelength(s) required by using a monochromatic light source to filter out other frequencies. FTIR has basically taken over from other forms of spectroscopy.

Differential Optical Absorption Spectroscopy (DOAS): is a method to determine concentrations of trace gases by measuring their specific narrow band absorption structures in the UV and visible spectral region.

Tuneable Diode Laser Absorption Spectroscopy (TDLAS): By scanning across a very narrow bandwidth in the IR region where no cross interferences occur, the absorption of the IR source by the targeted gas is proportional to the target gas concentration.

Photo-acoustic IR Spectrometer (PAS): This technique is a variant on the above and uses the fact that gases will absorb differently IR radiation which can be detected by sensitive microphones within a relatively small devise. The accuracy of ppb or ~0.5ppm is claimed, however, as would be expected these devices are prone to extraneous noise affecting them.

Radar Detection: For ammonia in vapours, radar detectors have been used as the Guided Radar signals are attenuated as the density of vapour increases. Radar detection is best for use in high pressure systems.

Gas sensors: Various types are in existence which all have benefits and drawbacks;

- **Metal Oxide Gas Sensors:** The ammonia sensors that have been manufactured in the largest quantities are without doubt metal-oxide gas sensors, mostly based on $C_{2-x}T_xO_3+z$ for measuring ammonia. They work by absorbing and de-absorbing the gas by cycling the temperature of the sensor and the changes in electrical conductivity are measured to determine the ammonia concentration. They are accurate to ~5ppm.
- **Catalytic Bead Ammonia Sensors:** Also known as Wheatstone Bridge LEL sensors. Ammonia sensitive field effect transistors are called GASFET (Gallium Arsenide Field Effect Transistor or Gas Sensitive Field Effect Transistor – depending which site you read). They use a palladium gate material and have a detection limit of 1 ppm. They have also been combined with polymers, see below. However, they are also sensitive to methane gas and at high concentrations their life may be limited to minutes or hours.
- **Conducting polymer gas detectors:** A polymer is used which reacts with the ammonia. First, there is an irreversible reaction between ammonia and the polymer and, secondly, ammonia can reversibly reduce the oxidized form of polypyrrole. The reduction of the polymer film causes a change in the conductivity of the material, making it a suitable material for resistometric or amperometric ammonia detection. However, these polymers cannot be easily regenerated. The lower detection limit of gas sensors based polymers is about 1 ppm.
- **Photo Ionisation Potential (PID):** Ammonia has an ionisation potential of 10.18eV and therefore measured using a PID. They can measure up to 10,000 ppm. A PID is not specific to ammonia and will measure other compounds.

Measurement of Ammonia in Solution

Many proposed test methods are based on environmental tests for NH_3 in soil or water. The ammonia is brought into solution by washing or distillation, and then the quantity can be determined by a range of wet chemical or instrumental methods.

In aqueous solution, ammonia exists in equilibrium between the molecular and ionised forms, with the degree of dissociation depending on the temperature and pH:

$$NH_3 + H_2O = NH_4^+ + OH^-$$
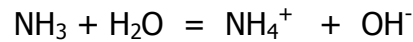
Some methods can selectively test for one form or the other, whilst other methods detect both forms. The units that results are reported in also vary between test methods and laboratories. Results may be reported as ammonia (NH_3), ammonium ion concentration (NH_4^+) or ammoniacal nitrogen (NH_3-N). Ammoniacal nitrogen (also called ammonia nitrogen) is the sum of both molecular and ionised forms of ammonia, expressed in terms of the nitrogen content.

Wet Chemistry methods: These types of methods are those usually preferred in European standards as they are describable and can be carried out generally using normal chemical apparatus. Nesslerisation would probably be considered the defacto method to use to calibrate/verify all the other methods of measuring ammonia. However, it has never been established by any validation testing to our knowledge. It is these chemical methods that also form the basis of the many test strips available, though with a considerable reduction in accuracy.

Nesslerisation (EPA 350.2): This is a classic chemical distillation method for the determination of ammonia-nitrogen and is the preferred method of choice by the USA EPA. There are three possible analytical methods, colorimetric (0.05 to 1.0mg NH_3-N/l), titrimetric (1 to 25mg/l) and an electrode method (0.05 to 1400mg/l).
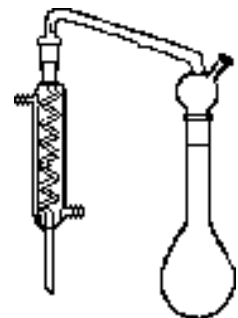
Basically the method requires adding sodium hydroxide to the material being tested, driving off the ammonia, this is then distilled off into boric acid and the ammonium salt in solution is measured. The conversion to ammonium salt is carried out in a Kjeldahl digestion flask as shown in the adjacent diagram. The level of ammonia is measured colorimetrically using the Nessler reagent.

The Nessler reagent consists of potassium tetraiodomercurate(II) in a dilute alkaline solution, normally sodium hydroxide. This reagent is toxic and potentially fatal on skin contact, inhalation or by ingestion[6]. It should not be released into drains or similar as it's very toxic to aquatic life.

Berthelot Reagent (EPA 350.1): This method is the same as the Nesslerisation method, except Berthelot reagent is used colorimetrically. Berthelot reagent is where alkaline phenol and hypochlorite reacts with ammonia to form indophenol blue, the colour depth being measured using colorimetrically.

Other Reagents: Various other reagents based on obtaining the blue indophenol blue, for example by using chloramine-T instead hypochlorite or by adding buffering

solutions. Another alternative is sodium nitroprusside with hypochlorite and phenol, again producing the indophenol blue colouring.

Ammonium Ion Selective Electrodes (ISE): These are used to measure ammonia content in solution, such as in the AiRRMonia system. The theory of operation is the ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode filling solution. In any given sample the partial pressure of ammonia will be proportional to its concentration. Dissolved NH_3 is gaseous and passes through the hydrophobic membrane of the ammonia ISE. The pH change of the electrolyte solution on the other side of the membrane caused by the diffused gas is sensed by the inner body of the ammonia electrode—a pH electrode. The pH change is relative to the amount of dissolved NH_3 present and can be measured with a pH or Ion meter capable of mV readings or, better yet, direct ion concentration. These devices need to be calibrated and can be difficult to get right. They are reported as being accurate to 1ppm, though the electrodes only last ~1 year.

Spectrophotometric ammonia detection: This process is basically using a chemical that changes colour in contact with ammonia. These may be in the form of pH papers on strips or more complex miniaturised measuring devices. Various reagents can be used such as fluorometric or indophenol blue, which are used to detect ammonia in fish tanks. They are generally claimed to be accurate to ~<6 to 50ppm and supplied for differing ranges of concentrations. The reagents used are;

- **Nessler reagent:** This is the best known technique, as described above but the reagent is highly toxic.
- **Berthelot reaction:** Another common reagent and similar alternatives. This can be altered to suit the material being tested, as described above.

Ion Chromatography: This is used to detect ammonium ions, by passing the solution through a column that will absorb ions at different rates depending on their charge. The ions passing out of the column can be detected by a variety of techniques such as electrochemical or spectrophotometric methods. Ion chromatography has the advantage of being able to differentiate between different forms of nitrogen species in solution.

Standards for ammonia testing

There are no performance standards against which NH_3 monitors can be certified, and there are no adopted methodologies for the certification of continuous NH_3 monitoring. While comparisons have been made between these methods based on the literature, few comparisons of accuracy and repeatability/reproducibility have been carried out to

our knowledge. ISO standards contain differing methods for differing materials, and even water quality methods allow a range of differing test procedures [7]

As part of a trial programme to assess the effects of ammonia on aircrete block manufacture, some comparisons in test methods were carried out. Table A shows the results of testing a range of ash samples using three different methods, all results are expressed as mg/kg NH_3. This clearly shows the differences associated with the different methods.

Result	Method	Control ash 1	Control ash 2	SCR ash 1	SCR ash 2	SCR ash 3
		mg/kg NH^3				
Water soluble ammonia	UV-visible light spectroscopy[1]	<1.21	<1.21	9.68	24.8	26.6
Water soluble ammonia	Ion chromatography[2]	0.98	0.19	26.3	33.3	30.3
Total ammonia	Steam distillation & titration[3]	5.07	2.25	32.8	40.5	41.2

Notes:

1. An extract using a water solid ratio of 1:1 is taken from the sample; the ammonia is then reacted with hypochlorite ions by alkaline hydrolysis in the presence of sodium nitroprusside to form indophenol blue, as modified version of the Berthelot reaction. The absorbance of this compound is then measured spectro-photometrically with a UV/Vis spectrophotometer and related to the ammonia concentration in the sample by means of a calibration curve.

2. Ammonia extracted using 10:1 water:solid ratio to BS EN12457-2[8] with the water extract being distilled with steam, see BS 6068-2 & ISO 5664, and then analysed by Ion Chromatography calibrated for ammonium ions in solution based on BS EN ISO 14911[9].

3. Extracted after alkalization of the ash with sodium hydroxide and then using steam distillation and then analysed by Ion Chromatography as in 2 above.

Table A - Ammonia concentrations from differing test methods

Clearly there is a need for a defacto test method by which the other techniques could be assessed. The wet chemical Nessler method would seem to be the strongest candidate, but drawback is the toxicity of the Nessler reagent. The Berthelot reaction would seem to be the next serious contender but with a somewhat reduced accuracy.

The gas sensors and light spectroscopy methods claim good accuracies, but no independent evidence has been found that supports the various manufactures claims. The simpler methods involving indicator papers and similar all appear to suffer with a considerable reduction in sensitivity in comparison with wet chemistry techniques, although these could be useful as a rapid qualitative or semi-quantitative test.

Limiting values for ammonia in fly ash

Differing limits for ammonia in fly ash are quoted throughout the EU. For example, the NH_3 limit in the Netherlands the requirement is for the average <75mg/kg with an absolute limit of 100mg/kg, absolute limits of 200mg/kg in Germany and Denmark and 100mg/kg in Spain apply. In general terms selective catalytic reduction (SCR) efficiency is about ~88% in removing the ammonia and the resulting content in the PFA is limited typically ranges from 10 to 100ppm. NH_3 removal rate is 99.7% efficient. However, there still can be enough to cause problems in the fly ash. NH_4HSO_4 can form if the catalyst is run at too low a temperature. This accounts for about 20% of the NO_x removal.

It is clear from all sources that ammonia in fly ash of >200mg/kg as NH_3 will cause odour problems with in concrete production in confined spaces and preferably it should be limited to <100mg/kg, where no effects would normally be noticed. However, for power station operational reasons, ammonia slip should be minimised and kept to <2ppmv, which equates to ~100kg/kg in the fly ash.

Effects on the manufacture of aircrete blocks

Primarily the problems with using ash containing excessive levels of ammonia are identical whether it is normal concrete or aircrete blocks being produced. The issue is that when a caustic alkali material, such as lime or cement, comes into contact with ammoniated fly ash in the presence of water, ammonia is released as a gas. The classic reaction of lime with ammonium salts would be;

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$$

For the SO_3 formed in the SCR and combined with ammonia, when this combination comes into contact with an alkali, e.g. cement or lime, a similar reaction takes place;

$$2NH_4HSO_4 + Ca(OH)_2 = 2NH_3 + CaSO_4 + 2H_2O$$
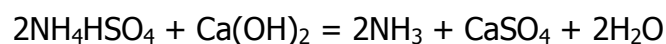
It is clear that ammonium salts are chemically weakly bound and in the presence of a stronger alkali the ammonium salt is easily decomposed releasing it as a gas. It is these basic reactions that are employed in the commercial ammonia removal plants.

Aircrete blocks are produced by casting a slurry of fly ash, cement, quicklime, calcium sulphate and aluminium powder in to a large open-topped mould. The mix is left to rise and set in a warm chamber, before being cut into blocks and cured in an autoclave. As aircrete block manufacture uses greater quantities of fly ash than traditional concrete manufacture, up to 80% of the material content may be fly ash, there is the potential for a significant release of ammonia in the manufacture of these blocks.

Hanson Building Products have undertaken a series of laboratory and factory trials using SCR fly ashes to manufacture Thermalite® aircrete blocks. The aim was to determine what effect such ash would have on the manufacturing process and products, and what an acceptable ammonia limit may be.

When small-scale aircrete mixes were prepared in the laboratory using SCR fly ash with a high ammonia level (~340 mg/kg NH_3), a peak reading of 80ppmv airborne NH_3 was detected above a freshly cast mix. This is well above the exposure limits and at a level likely to cause rapid irritation to the eyes and respiratory tract. This clearly shows the potential health and safety risk from ammonia contaminated raw materials.

A series of factory trials were conducted using SCR fly ash with a low ammonia level (~40 mg/kg NH_3), using around 100 tonnes of ash in total. This ash was not found to have any detrimental effects on the manufacturing process, for example the setting time of the product. Airborne ammonia levels were monitored around the manufacturing plant during the trials, but nothing significant was detected. Blocks made with this SCR fly ash passed all of the relevant product standard tests. The compressive strength, density, thermal conductivity and drying shrinkage results were comparable to those for blocks made using a non-SCR fly ash.

The laboratory results shown in Table B indicate that even high levels of ammonia in fly ash are removed from aircrete by the final stage of the manufacturing process, where the blocks are cured in a high-pressure steam autoclave. Therefore there would be no risk to end users of an aircrete product made using ammoniated fly ash.

Sample	NH_3 (mg/kg)
Control fly ash	1.2
Aircrete made with control fly ash	3.0
Non-SCR fly ash	342
Aircrete made with SCR fly ash	1.8

Table B - Ammonia found in aircrete

Therefore, the use of SCR fly ash for the manufacture of aircrete does not appear to have any detrimental effect on the finished product, or present any risk to the end user. However, it could cause a significant health and safety risk in the manufacturing plant unless carefully monitored and controlled. The limits of 100-200 mg/kg ammonia suggested in some EU countries could be unacceptable for the UK aircrete market. Further work is required to determine a maximum NH_3 limit, based on an appropriate and practicable test method.

Effects on the manufacture of concrete

The Danish Technological Institute produced a series of reports[3] on the effects of ammoniated fly ash on concrete, emissions rate, etc. They concluded that fly ash with up to 200mg/kg as NH_3 will not cause concentrations of ammonia hazardous to health in well ventilated rooms and the ammonia will have evaporated to such an extent after a few months as to not cause indoor climate problems.

Rathbone and Robl[10] demonstrated that ammonia is lost from mortars at a higher rate for higher water-cement ratios, with a rapid rate of emission for the first 24 hours, followed by a much slower rate thereafter. This is similar to what was observed for aqueous solutions of ammonia. The total emissions were directly proportional to the initial concentrations and ventilating the samples increased the rate of ammonia from the mortars. They concluded that for concretes containing 20% fly ash of cement, ammonia levels in fly ash could be as high as 240 to 375 mg/kg as NH_3 for the full range of common concrete mixes. They also concluded that 15% of the ammonia was lost after 40 minutes of mixing the concrete. Approximately 50% of the ammonia in a concrete slab had dissipated after 1 month, but air concentrations in the air were below 1-2 ppm after several days of curing. The problems with ammoniated ash concrete are most likely to occur within 3 to 5 hours of placing, e.g. during the placement and finishing processes.

Removing ammonia from fly ash

Bittner et al[11] describes one possible method of removal of ammonia using the STI patented process. This uses lime and water as reactants to liberate the ammonia from the ash by mixing and thereafter drying. With the correct proportioning of lime and water the considerable majority of the ammonia is released within 2 to 3 minutes, making this process an effective solution to ammoniated ash.

The STI system operated by Lafarge, has proven particularly effective at the Aberthaw power station, where ammonia injection is used to improve precipitator efficiently only i.e. has no SCR unit. This results in relatively high NH_3 levels, often above 200mg/kg in the fly ash. After processing very low levels of NH_3 remain in the fly ash, making it suitable for use in cement and concrete manufacture.

Other methods of removing ammonia seem to rely on heat treatment such as fluidised bed to drive off the ammonia or adding compounds to mortar or concrete to supress the ammonia release. Heat treatment methods are usually associated with carbon burn out techniques[12] of fly ash and can remove ammonia down to <5ppm. To the knowledge of the authors no other ammonia specific systems than the STI ammonium removal system are in use world-wide.

Conclusions

In order to define acceptable limit values for ammonia in fly ash, it is clear that industry agreed test method is needed, thereby making compliance and sensible comparisons possible. At this stage it has proven impossible to obtain a consensus as to which method is considered the most appropriate for fly ash. Liaison throughout the European ash producer's industry trade association and users of fly ash will continue until an appropriate method is agreed.

[1] DIRECTIVE 2001/80/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2001 on the limitation of emissions of certain pollutants into the air from large combustion plants, EU Commission 2001.

United Kingdom National Emission Reduction Plan for implementation of the revised Large Combustion Plants Directive (2001/80/EC), February 2006, UPDATE No. 6, 14 July 2011. See http://www.defra.gov.uk/environment/quality/industrial/eu-international/lcpd/ for details.

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[6] See http://chemexper.otavachemicals.com/chemicals/supplier/cas/7783-33-7.html for Health and Safety information. Accessed 29 Nov 2011. CAS registry Number 7783-33-7

[7] BS 6068-2.7:1984, ISO 5664-1984Water quality. Physical, chemical and biochemical methods. Determination of ammonium: distillation and titration method

BS 6068-2.10:1984, ISO 6778-1984 Water quality. Physical, chemical and biochemical methods. Determination of ammonium: potentiometric method

BS 6068-2.11:1984, ISO 7150-1:1984 Water quality. Physical, chemical and biochemical methods. Determination of ammonium: manual spectrometric method

[8] BS EN 12457-1:2002. Characterisation of waste. Leaching. Compliance test for leaching of granular waste materials and sludges. One stage batch test at a liquid to solid ratio of 2 l/kg for materials with high solid content and with particle size below 4 mm (without or with size reduction)

[9] BS EN ISO 14911:1999. Water quality. Determination of dissolved Li$u+, Na.

[10] Rathbone R F, Robl T L, Study of the Effects of Post-Combustion Ammonia Injection on Fly Ash Quality: Characterization of Ammonia Release from Concrete and Mortars Containing Fly Ash as a Pozzolanic Admixture, University of Kentucky Center for Applied Energy research, Kentucky, DE-FC26-00NT40908, 2003.

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