Principal of Operation
Selective catalytic reduction (SCR) for NOx control

What are Nitrogen Oxides?

- NOx emissions are the product of every air-fed combustion process such as
  - Cars
  - Industrial Processes
  - Power Plants
  - Solid Waste Disposal
- Nitric Oxide and Nitrogen Dioxide are a product of high temperature combustion.
- Nitrogen Dioxide is the compound largely responsible for the orange to reddish/ brown color NOx imparts to the air.

How do they effect us?
NOx emissions are suspected of contributing directly and indirectly to several atmospheric processes that are known to be degrading the environment.

–Acid Rain
–Forest and Vegetation Decline
–Changes to Ozone Layer

The US Clean Air Act has defined stringent guidelines to regulate the emissions of NOx, carbon monoxide and unburned hydrocarbons. Under this act the EPA has established air quality standards but the requirements for specific sites are defined at the state and local level. Areas that do not meet these standards are defined as non-attainment versus areas that do which are referred to as attainment areas. Acquiring an operation permit for new installations will be dependent upon this classification. Areas that are classified as non-attainment will not be allowed to install new NOx generating sources without reductions in other areas. The net result being no increase in emissions. If this is not possible then Emission Reduction Credits (ERC) must be acquired from sources within the same area. ERC's therefore are acquired by reducing your emission sources below required levels and a monetary value is placed on them and sold to sources which cannot economically or technically comply with emission standards.

The 22 State Ozone Transport Rule indicates that the EPA wants an 80% overall reduction in NOx by the year 2003, while the states have proposed approximately 60%. The differences in these reduction levels are comparative to what can be achieved with the SCR and the SNCR processes. The SNCR process does not involve the use of catalyst and reduction is accomplished via ammonia injection.

How does ammonia reduce Nitrogen Oxide?
Injection of ammonia in the flue gas in presence of a catalyst which causes chemical reactions that convert the NOx to free nitrogen and water vapor.

–NO
4 NO + 4 NH3 + O2 ----------- 4 N2 + 6 H2O

–NO2
4 NO2 + 8 NH3 + 2 O2 ----------- 6 N2 + 12 H2O

Temperatures for ideal de-nitrification must take place between 392 and 1022 degree Fahrenheit. Temperatures below 400 can cause the formation of ammonia salts. Temperatures above 850 can cause a reverse reaction where ammonia is converted back into NOx.

There are various operation modes of a combined cycle power plant, which inherently require varying amounts of ammonia to be injected into the flue gas stream as part of the SCR system. In SCR systems, ammonia or a compound of ammonia is used as the reducing agent and is injected into the flue gas stream, passing over a catalyst. NOx emission reductions over 80- 90% are achieved. Temperatures for ideal de-nitrification must take place between 392 °F and 1022 °F. Temperatures below 400 °F can cause the formation of ammonia salts. Temperatures above 850°F can cause a reverse reaction where ammonia is converted back into NOx.

The efficiency of SCR process reactions allows very close and effective reagent injection-control based on feedback, of measured NOx concentrations in the flue gas at the economizer outlet. The ammonia injection grid is located in the ductwork leading to the SCR catalyst, far enough upstream to ensure optimum gas and reagent distribution across the catalyst cross-section.

The catalysts can have different compositions: based on titanium oxide, iron oxide or activated carbon. Most catalysts in use in coal-fired plants consist of vanadium (active catalyst) and titanium (used to disperse and support the vanadium) mixture. However, the final catalyst composition can consist of many active metals and support materials to meet specific requirements in each SCR installation. Catalyst geometry may typically be a flat plate or honeycomb. A moving bed is used for granular activated carbon. German experience shows that plate types generally have a higher resistance to deposition and erosion than honeycombs.

To accommodate NOx reduction, an on line feedback control of the process exhaust data or injection mapping functions is typically implemented. The amount of ammonia injected is somewhat proportional, although not linear due to residual delays caused by absorption, to the overall NOx reduction due to the reaction of the ammonia with the installed catalyst material. Over-injection of ammonia will greatly reduce the NOx emissions but will lead to what is called "ammonia slip" which is also typically an operational parameter specified in the CEMS (Continuous Emission Monitoring System) specifications. Since these systems are very interdependent and ultimately determine the plants overall operational capacity and regulatory compliance, it is vital that each component have adequate, reliable and proper controls.

Selection of the Reducing Agent:

Anhydrous ammonia is the preferred reducing agent in SCR applications. However, site and customer specific regulatory and safety concerns have necessitated use of alternative anhydrous ammonia derivatives each with some advantage/disadvantages.

Anhydrous Ammonia

Anhydrous ammonia is the compound formed by the combination of the two gaseous elements, nitrogen and hydrogen, in the proportion of one part nitrogen to three parts hydrogen by volume. On a weight basis, the ratio is fourteen parts of nitrogen to three parts of hydrogen, or about 82% nitrogen and 18% hydrogen.

At atmospheric temperatures and pressures, anhydrous ammonia is a pungent colorless gas. Anhydrous Ammonia boils at -28°F and freezes to a white crystalline mass at -107.9°F. When heated above its critical temperature of 270.3°F ammonia exists only as a vapor regardless of the pressure. Between the melting and critical points, liquid ammonia exerts a vapor pressure, which increases with rising temperature. When liquid ammonia is in a closed container it is in equilibrium with ammonia vapor and the pressure within the container bears a definite relationship to the temperature. Ammonia liquid is lighter than water, having a density of 42.57 pounds per cubic foot at -28°F., while as a vapor, ammonia is lighter than air, its relative density being 0.5970 compared to air at atmospheric pressure and a temperature of 32 °F. Under the latter conditions, one pound of ammonia vapor occupies a volume of 20.78 cubic feet. At 7O °F. and atmospheric pressure, one pound of ammonia occupies a volume of 22.5 cubic feet and yields 45 cubic feet of dissociated gas at a ratio of 25% nitrogen and 75% hydrogen.

Ammonium Hydroxide 29% to 19% Solutions

Aqua ammonia, aqueous ammonia and ammonium hydroxide are synonymous terms referring to a solution of ammonia in water. The chemical formula for ammonium hydroxide is NH_4OH. Ammonia dissolved in water is present principally as the ion NH_4^+. Non-ionized molecular NH_4OH, sometimes referred to as an associated form of ammonium hydroxide, is also present. Hydrated molecules of NH_3 may also exist as $NH_3 \cdot H20$ or $NH_3 \cdot 2H20$. Ammonia dissolved in water is commonly referred to as 'aqua ammonia'.

The grade or strength of Ammonium Hydroxide usually available commercially is 26- Degree Baumé. However, any strength product can be custom blended to meet the

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project requirements. The Baumé reading refers to a specific gravity scale. A 26- Degree Baumé solution is equivalent to 29.4% by weight of ammonia dissolved in water. Since the Baumé reading varies with temperature, the reading is standardized at 60° F. The density of the material compared to water is 0.8974.

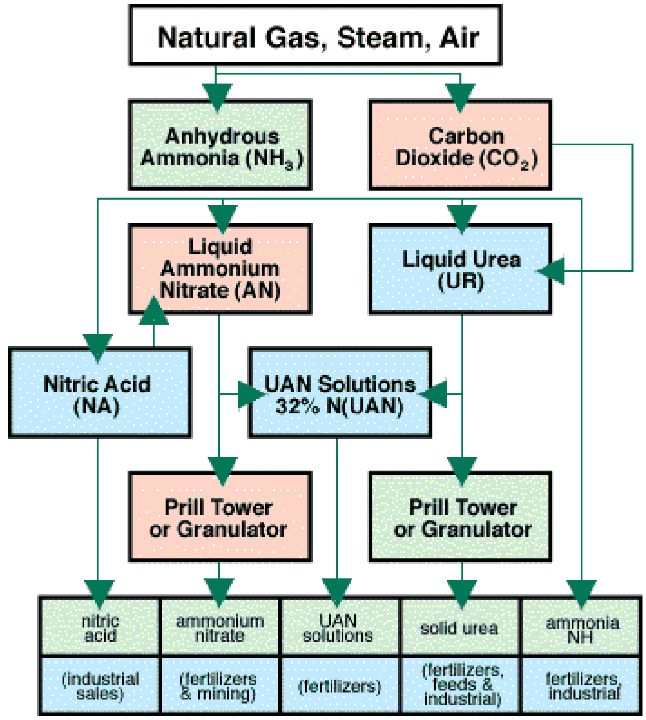
Aqua ammonia is corrosive to copper, copper alloys, aluminum alloys and Galvanized surfaces. Aqua ammonia is an excellent acid neutralizer. Its pH varies with concentration. Typical values are 11.7 at 1%, 12 .2 at 5%, 12.4 at 10% and 13.5 at 30%. The freezing point of a 26- Degree Baumé solution is about -112° F.

An Aqua solution has a vapor pressure, which varies with temperature. At ambient temperatures, the vapor pressure of 26- degree Baumé material just about equals atmospheric pressure. This permits the material to be shipped and stored in "non-pressurized" containers and is the reason why this is the strongest strength material generally available in the marketplace. Aqua should be stored in a closed container and kept cool, otherwise, the ammonia gas will come out of solution and the material strength will be reduced.

Urea Prill and Urea 40 to 50% Solutions

The commercial synthesis of urea involves the combination of ammonia and carbon dioxide at high pressure to form ammonium carbamate, which is subsequently dehydrated by the application of heat to form urea and water. Reaction 1 is fast and exothermic and essentially goes to completion under the reaction conditions used industrially. Reaction 2 is slower and endothermic and does not go to completion. The conversion (on a CO_2 basis) is usually in the order of 50-80%. The conversion increases with increasing temperature and NH_3/CO_2 ratio and decreases with increasing H_2O/CO_2 ratio.

$2NH_3$	$+ CO_2$	NH_2COONH_4	$CO(NH_2)_2 +$	H_2O
Ammonia	Carbon Dioxide	Ammonium Carbamate	Urea	Water



One ton of ammonia is 1.72 tons of urea (urea is about 56% ammonia- in terms of Nitrogen content). For 1 ton of ammonia/ hr, the process will need approx. 1.72 tons of urea/hr or just over 41 tons of urea/ day. (Conversions may require more or less urea depending on the quantity of ammonia made per ton of urea. These numbers above are internal conversions based on Nitrogen content). There are two kinds of trucks available to deliver urea, hopper or pneumatic. Both carry approximately 25-tons/ truck and the cost of pneumatic usually exceeds hoppers, sometimes by as much as double. Urea can be stored in a variety of ways: silos or warehouses are two common methods.

Advantages and Disadvantages of Reducing Agents:

In the SCR process the use of ammonia is essential, however, the form of ammonia to be used can be determined upon evaluation of inherent advantages/disadvantages. Anhydrous ammonia is the cheapest and requires a very simple system to be delivered to the SCR process. With this fact, why would we even consider other alternatives? The EPA in 1994 classified anhydrous ammonia and ammonium Hydroxide above 20% concentration a regulated toxic substance and fears of this have driven many to go with alternatives. As with any toxic substances, there are EPA requirements to develop and implement process safety and risk management programs to address and prepare personnel in the worst case scenario of product releases. Ammonia Hydroxide @ 19% concentration is a viable solution without the regulatory requirements however, it is more costly than anhydrous ammonia, which is 100% concentration, and requires additional system expenses in the storage and delivery to the SCR. Storage capacity due to the dilution of the ammonia increases significantly and the requirement for containment areas for possibility of liquid releases is required.

In response to recent concerns over storing and handling ammonia other methods are being researched and are becoming commercially available. The concept behind this technology is to take a product referred to as Urea, which is available in pellet form, and convert it on site to ammonia. This eliminates the requirement for large storage of ammonia product and subsequent handling to have it delivered and loaded. The most unfortunate aspect of this technology is that the elimination of the safety concerns comes at additional cost in the process and system complexity. In most such processes the use of de-mineralized water is required and for large consumption systems the availability of ammonia, in case of system failure, could be a concern. These systems typically have higher associated operating and maintenance costs than a simple storage and delivery systems. System failure and interruptions will result in shut down of the SCR system due to insufficient inventory to operate.

The concept of using Urea is however very effective in addressing the safety issues associated with handling ammonia. An alternative to the Urea conversion process is to simply acquire it in liquid form and have it injected directly into the SCR process. This system is very similar to the Ammonium Hydroxide system without the inherent EPA guideline and safety issues with handling and storing the product and eliminates the requirement for additional systems to convert the pelletized Urea. Increased product cost and storage capacity due to the dilution of the urea and the requirement for containment areas for possibility of liquid releases is required.

Since Urea is manufactured from ammonia stock, it inherently has the necessary chemical components to facilitate the catalyst reaction required to reduce the NOx emissions without the concerns over dealing with ammonia directly. As this alternative is viable it seems somewhat unnecessary to incur additional cost when we look at the numerous industries and uses of ammonia in our country. The agricultural industries are the major users of ammonia representing nearly 80% of all ammonia produced in the US. It is a very valuable source of nitrogen and is essential in plant growth. It is estimated that nearly 4 million tons of ammonia was applied directly to the soil in 1983. Ammonia is used in the production of fertilizer, an anti-fungal agent on certain fruits and a preservative for storage of high moisture corn. It is used in the manufacturing of nitric acid, pharmaceuticals, vitamins, cosmetics, nylon, acrylics and certain plastics. It is used in the mining industry for extraction of metals such as copper and nickel. The petroleum industry uses it to neutralize the acid constituents of crude oil and for protection of equipment from corrosion. It is used in water and wastewater treatment for pH control, in photomechanical processes as a developing agent, in the rubber industry to prevent premature coagulation, in the food and beverage industry as a source of nitrogen needed by yeast and microorganisms and is widely used as a refrigerant in industrial refrigeration systems.

Product	Market Reference	Freight Range/ton	Delivered Price/ton	Equivalent Ammonia
Anhydrous Ammonia	New Orleans (Green Markets) NOLA $180	$50-$60	NOLA plus $60-70 $230-$240	100%
Ammonium Hydroxide 29%	Baltimore	Included	$280 to $310	29%
Ammonium Hydroxide 19%	Baltimore	Included	$310 to $340	19%
Urea Prill	New Orleans (Green Markets) NOLA $155	$65-$75	NOLA plus $65-$75 $220-$230	56%
Urea Liquor 50%	Baltimore	Included	$250-$260	28%

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