AMMONIA - "THE REST OF THE STORY"

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There is rapidly growing interest in the use of ammonia as a neutralizing agent for acid discharges associated with coal mining. Ammonia is a very cost effective and operationally efficient chemical for the coal industry and it has solved several difficult water treatment problems. -Some State regulatory agencies, however, have not responded enthusiastically to requests by the industry to use ammonia. There are concerns that ammonia cannot be handled safely with out harming aquatic life and without generating acidity downstream of the discharge point. This forum, The Seventh Annual West Virginia Surface Mine Drainage Taskforce Symposium, is the proper place to share what we know about ammonia neutralization and to clear-up the misconceptions.

Ammonia is a component of nature's nitrogen cycle but for agricultural and industrial use, it is synthesized from nitrogen and hydrogen. It is a stable, pungent, colorless gas at ordinary temperature and pressure. When compressed and cooled, ammonia condenses to a colorless liquid about 60% as dense as water.

Ammonia is typically stored in pressure vessels (Fig. 1) although it can be stored in a refrigerated state. Pressures in an ammonia storage tank are usually quite low. At 70^0 F, ammonia has a pressure of 114 psig and weighs 5.08 pounds per gallon. Liquid ammonia boils at -28^0 F, freezes at -107^0 F, and is classified by the U. S. Department of Transportation as a non-flammable compressed gas.

Ammonia vapor is not poisonous, but due to its high solubility in water, it has a very irritating action on the mucous membrane of the eyes, nose, throat, and lungs. The very pungent odor of ammonia serves as an early warning signal and can be detected at levels as low as 53 parts of ammonia per million parts of air. Liquid ammonia vaporizes readily and has a great affinity for water. If improperly handled, liquid ammonia can cause severe injury to the skin by freezing and subjecting it to caustic action. The storage and prescribed use of ammonia makes contact with the liquid very unlikely.

Ammonia is a biologically active compound present in most waters as a normal degradation product of nitrogenous organic matter. When ammonia dissolves in water, most of the ammonia reacts with the water to form ammonium ions (NH_4^+). A chemical equilibrium is established which contains un-ionized ammonia (NH^3), ionized ammonia (NH_4^+), and hydroxide ions (OH^-). The following equation expresses the equilibrium of these chemical species:

$$NH_3 + H_2O \rightleftharpoons NH_3 \cdot H_2O \rightleftharpoons NH_4^+ + OH^-$$

NH_3 represents ammonia gas combining with water. $NH_3 . H_2O$ represents the un-ionized ammonia molecule which is loosely attached to a water molecule. Dissolved un-ionized ammonia is represented by NH_3 for convenience. The ionized form of ammonia is represented by NH_4^+. The term total ammonia refers to the sum of these (NH_3 + NH_4^+).

The first major concern expressed by some regulatory agencies is that ammonia can be toxic to fish and other forms of aquatic life. Early studies showed that toxicity varied with the pH of the water and subsequent studies demonstrated that it is the un-ionized fraction of ammonia in solution which is toxic. It was also shown that temperature and ionic strength of the solution affect the NH_3 concentration. In most natural waters, the pH range is such that the NH_4^+ fraction predominates. It requires highly alkaline waters for the NH_3 fraction to reach toxic levels. The following formula can be used to calculate the concentration of un-ionized ammonia in solution:

$$\text{un-ionized ammonia} = 1.2 \frac{\text{total ammonia-N}}{1 + 10^{(pK_a - pH)}}$$

$$\text{Where:} \quad pK_a = 0.902 + \left(\frac{2730}{273.2 + T}\right)$$

$$T = {}^\circ \text{ Centigrade}$$

Levels of un-ionized ammonia in the range of .20 mg/l to 2 mg/l have been shown to be toxic to some species of freshwater aquatic life. The West Virginia in stream standard allows a maximum concentration of .02 mg/l un-ionized ammonia in trout waters and .50 mg/l in all other waters. The trout water criteria is 1/10th of the lower value of the toxic effect range. No limits are set by USPHS Drinking Water Standards or the WHO International Standards. In fact, ammonia is used in waterworks to from chloramines for sterilization and residual action in water. Despite the very conservative standards, experience has shown that ammonia can be used without adverse impacts to the aquatic environment.

In the fall of 1985, the West Virginia DNR sent two aquatic biologists to sample the receiving stream below the discharge of a Davis Trucking Company mine site where ammonia had been used to treat an acid discharge for over two years. Samples of benthic or bottom dwelling communities were sampled because of their low tolerance to pollution and their slow rate of recovery once destroyed. Samples were gathered upstream and downstream of the discharge and in a nearby tributary to the receiving stream which is unaffected by mining. A report of these findings has not been published but field observations revealed a well diversified benthos which contained several species very intolerant of pollution. There were stonefly larva, cadisfly nymphs and crawfish in all of the samples. The biological desert in the path of an ammonia discharge was not found.

The second major concern of some regulatory agency personnel stems from an idea published in "Reclamation News & Views" from the University of Kentucky, College of Agriculture. The authors suggest that nitrifying bacteria will oxidize NH_4^+ in an aerobic environment to NO_3^- liberating two H^+ ions in the process and, thereby, increase the total acidity. The authors feel that this acidification might not be immediately apparent and that it would take place somewhere downstream. Since this article was published, there have been many people looking downstream for this acidification. To my knowledge, no one has found it.

There are several important factors which determine the rate of ammonium oxidation. Nitrifying bacteria are particularly sensitive to pH and are most active in slightly alkaline or neutral conditions. They are severely inhibited by pH below 5.5 and the reaction barely proceeds below 4.5 pH. The optimum temperature for the reaction is near 90^0 F and it is very slow below 40^0 F. In most head-waters streams, this oxidation reaction would be very slow if it took place at all.

Nitrogen exists in the environment in many oxidation states. Microorganisms interconvert these forms of nitrogen by various oxidative or reductive pathways (Fig. 2) thus, there exists within the environment the potential to remove excess ammonium as gaseous nitrogen. If this capacity did not exist, the runoff from the 12.5 million tons of ammonia used annually in American agriculture would have acidified all of our surface water.

In order to compare ammonia with other commonly used neutralizing agents, it is necessary to understand equivalency. one equivalent weight of an acid will completely react with one equivalent weight of an base. This does not mean that one pound of an acid will completely react with ond pound of a base. One equivalent weight of sulfuric acid, for example, is 49.04 which is equivalent to 17.00 for ammonia. Once the equivalent weights have been determined for the commonly used bases, they can be easily compared.

CHEMICAL	FORMULA	EQUIVALENT WEIGHT	1 POUND NH_3 EQUALS
Ammonia	NH_3	17.00	1.00 Pound
Calcium Carbonate	$CaCO_3$	50.05	2.94 Pounds
Caustic Soda	NaOH	40.00	2.35 Pounds
Hydrated Lime	$Ca(OH)_2$	37.05	2.18 Pounds
Soda Ash	Na_2CO_3	53.00	3.12 Pounds

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Neutralization of an acid occurs when it is combined with a base. An acid destroys the basic properties of a base and vice versa. The neutralization reaction usually results in the formation of a salt as shown in the following reaction of ammonia and sulfuric acid:

$$\underset{\text{(Base)}}{2NH_3} + \underset{\text{(Acid)}}{H_2SO_4} \longrightarrow \underset{\text{(Salt)}}{(NH_4)_2SO_4}$$

If metallic salts are present in aqueous solution, ammonia will react with certain of them to produce metal hydroxides. A typical reaction is shown below:

$$2H_2O + FeSO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4 + Fe(OH)_2$$

This combination of reactions expresses what happens when ammonia is used in the treatment of acid mine drainage. The acid is neutralized by the base and the metals are precipitated as hydroxides. Ammonia adds no additional salts to the solution and does not create a solid precipitate or sludge which must be handled later as a bulk waste. The metal precipitates are gelatinous and they provide the added benefit of a flocculant clearing the solution of suspended clays and other fine particles as they settle. When the hydroxides precipitated by ammonia accumulate to the clean-out point, they can be pumped out rather than dug out with a dragline.

Ammonia provides fast neutralization because it enters into the reaction as a vapor or a liquid. Solid neutralizers must first dissolve before they become active. During that process, significant amounts of the solids become armored with metal hydroxides and add to the sludge without reacting. The rapid and complete reaction of ammonia makes accurate control possible with much less waste.

Ammonia is very cost competitive with the other popular neutralizers. The following table shows the equivalent costs:

CHEMICAL	COST/LB.	EQUIVALENT	EQUIVALENT COST
NH_3	$0.24	1.00	$0.24
$CaCO_3$	0.0075	2.94	0.02
NaOH	0.14	2.35	0.329
$Ca(OH)_2$	0.06	2.18	0.125
Na_2CO_3	0.15	3.12	0.468

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There are several significant operational advantages to ammonia which further improve the costs. The pressure tank (Fig. 1) is provided by the supplier for an annual rental fee of $1.00. Ammonia will not freeze, gel, or otherwise solidify at any temperatures encountered on the mine site so it can be used easily all year. Ammonia is a compressed gas so it flows under its own pressure and does not have to be pumped or gravity fed. This feature allows the storage tank to be set in a convenient place without being constrained by power supply or topography. Since ammonia is under pressure, no additional agitation or mixing is required. There are no heavy bags or drums to carry or waste due to spillage, water damage or armoring. The ammonia flows from its storage tank through a pipe directly into the treatment site so there are very few chances of accident or injury. The user never comes in contact with the chemical because the tank is filled by the supplier and neutralization is accomplished by simply opening and closing a valve. The reduction in manhours spent treating water with an ammonia system can also be significant.

AMMONIA STORAGE TANK
Figure 1

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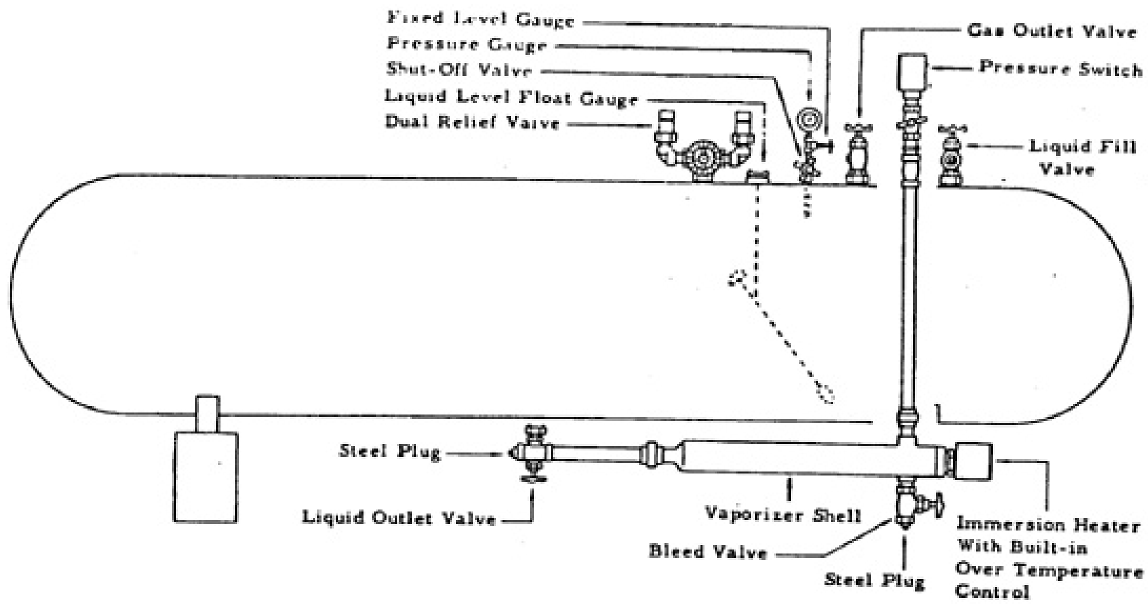
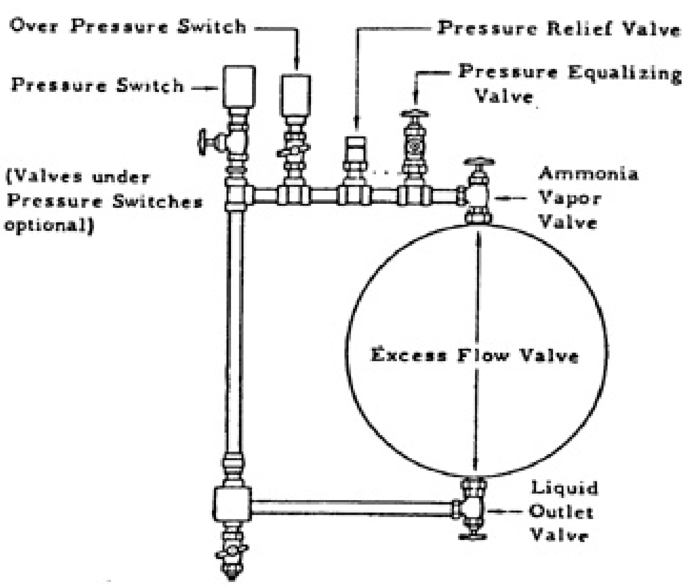
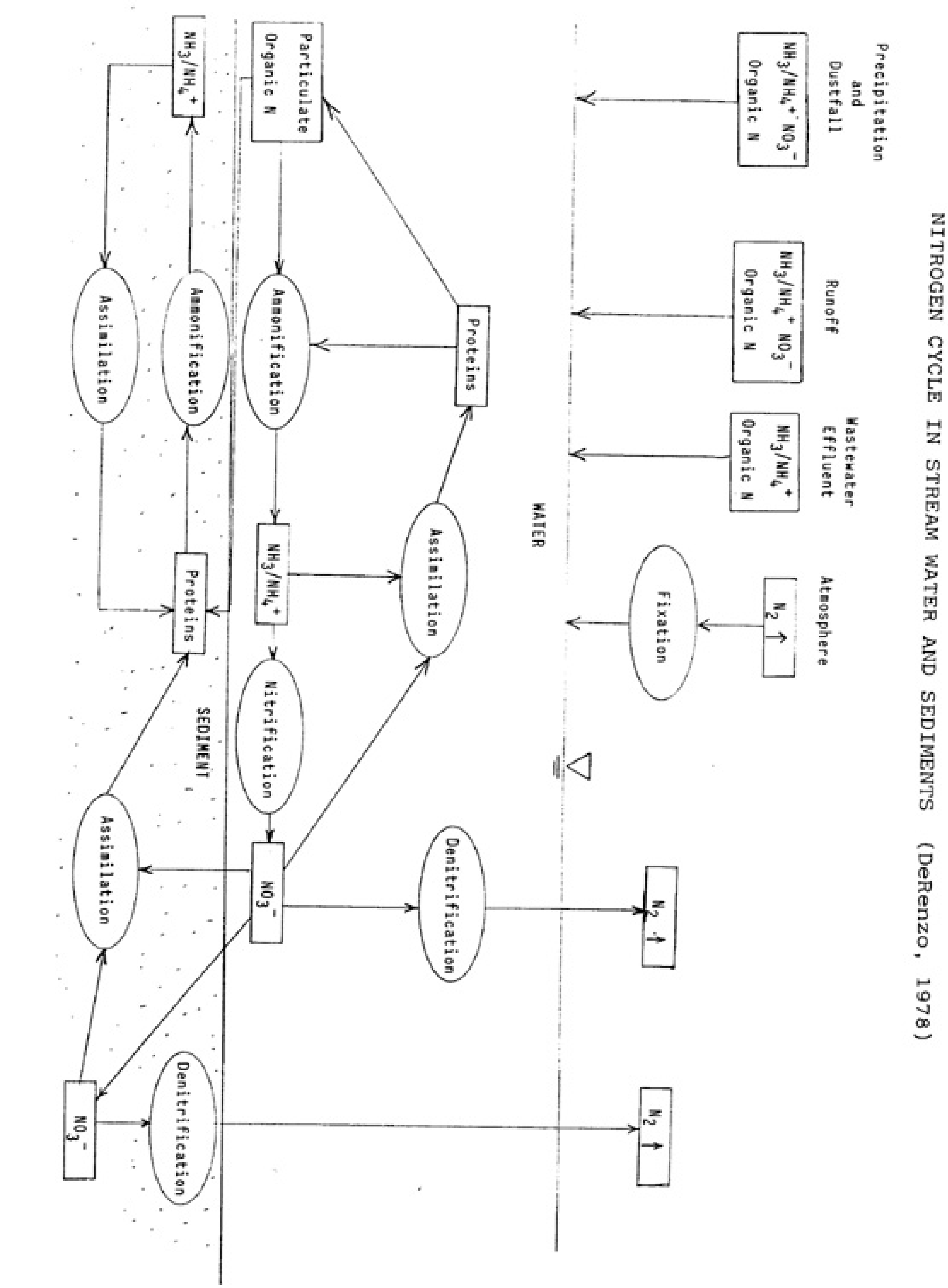




Ammonia treatment lends itself to automation which will further reduce treatment costs. A pH analyzer can be installed to monitor the pH of the discharge and to operate a solenoid valve which will add ammonia as required by changes in pH. A automated system will cost about $1,800.00 and will need to be custom fitted for each site but it will save many times its cost by preventing overtreating and reducing labor.

Ammonia can also be used in coal preparation plants safely and without odor. Ammonia will not adversely affect the flocculants used in the plant and the gelatinous precipitate will assist clearing the fines. Ammonia can be added as a vapor when close control is required or as a liquid when rapid neutralization is desired. This flexibility is a great advantage for plants which wash several different seams of coal each having a different effect on pH control.

The concerns expressed over the use of ammonia in the coal fields have been exaggerated. Ammonia is a very cost effective neutralizer in the preparation plant and on the mine site. It is operationally very simple to use and handle safely. It can be used with automatic controllers which assure close pH control even at night, on weekends and during storms. Ammonia can be used responsibly without environmental harm to aquatic communities directly below the discharge point or further downstream. Ammonia is a natural by-product of decomposition and nature is well equipped to-use it and to recycle it.



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