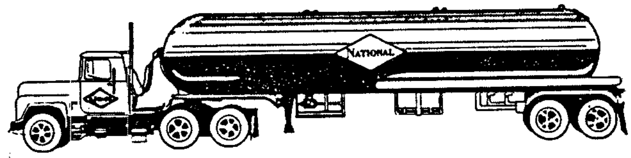
ANHYDROUS AMMONIA FOR ACID MINE DRAINAGE



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ANHYDROUS AMMONIA FOR ACID MINE DRAINAGE

There is a rapidly growing interest in the use of anhydrous 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 its use has solved several difficult water treatment problems. The Philadelphia based National Ammonia Company, a member of the West Virginia Mining & Reclamation Association, has been supplying ammonia to the mining industry for many years. Our service also includes the lease of one or more 1000 gallon stationary storage tanks, ammonia vaporizers and ammonia associated hardware and safety items. The cost of leasing an ammonia storage tank depends on ammonia usage and may be as little as one dollar per year. Ammonia deliveries are made by trained professionals, driving our own fleet of well maintained trucks. We offer ammonia safety training to our customers at no charge.

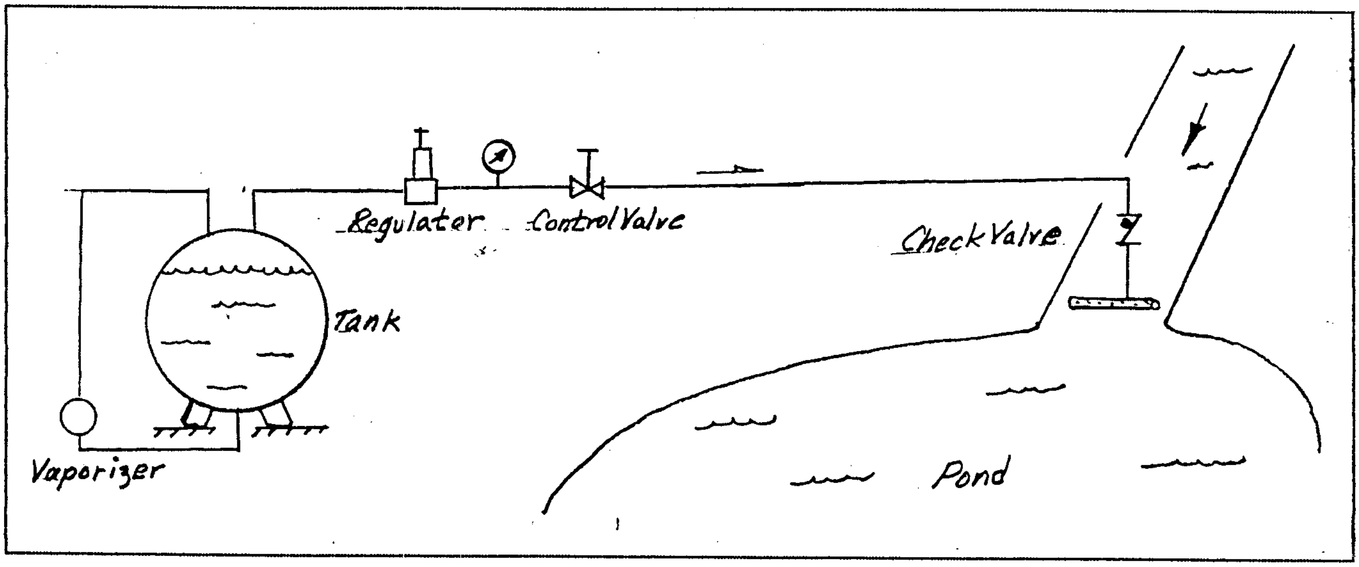
The information which follows has been compiled from many sources. I have relied on the experience of many of our customers in the water treatment field to formulate the following ammonia treatment guide. Experience has shown that, because of the many variables involved in the treatment of acidic water, it is necessary to analyze the conditions at your individual site to determine if the use of anhydrous ammonia is the right treatment for you.

Anhydrous ammonia is transported and stored as a liquid in carbon steel pressure vessels rated for 250 psig. Because the ammonia liquid has a very high coefficient of expansion, a 15% vapor space is always left at the top of a vessel. This allows the vessel to be exposed only to the vapor pressure of the liquid and not to a hydrostatic pressure which could be extremely high. The vapor pressure of liquid ammonia at 70°F is relatively low; about 114 psig, but is high enough at normal ambient temperatures to permit its use as a source of pressure for feeding purposes. Therefore a pump is not necessary. Ammonia has very narrow limits of flammability (16 to 25% by volume in air) and is difficult to ignite. Based on this, it has been classified by the U.S.D.O.T. as a Nonflammable Gas. Additional technical information on ammonia is available in the pamphlet "Storage & Handling of Anhydrous Ammonia".

Historically, the cost of ammonia has been low and stable and very competitive with other popular neutralizers. Also, there are several significant operational advantages to the use of ammonia. Ammonia will not freeze, gel or solidify at low temperatures so it may be used in all seasons. As a compressed gas, it does not have to be pumped or gravity fed. A storage tank may be located for convenience and not for reasons imposed by power sources or topography. Ammonia is homogenious and requires no mixing or additional agitation. There are no heavy bags or drums to transport or storage facilities needed. Once a tank is in place, no one, other than our trained drivers, need come in contact with the chemical. Valves are simply opened or closed. There are few chances for accident or injury. The reduction in man-hours which are made possible by using ammonia can be quite significant. The rapid and complete reaction of the ammonia with the water makes accurate feed control possible resulting in minimal waste.

The earliest method of ammonia treatment utilized a floating or surface injection point on a pond. The ammonia was fed in vapor form. A solenoid valve was located in the line feeding the injection point and the valve was opened and closed by a pH controller located at the pond discharge point. The valve opened when the pH reached a low set point and closed when the pH reached a high set point. Although this method is still used where the site has several ponds in series, it does present some problems where only one pond is involved. Because the ammonia concentration is always greater at the injection point than it is at the pond discharge point, the water between the injection point and the pond discharge point is always over treated. An ammonia water mixture is less dense than water alone and will tend to remain on the surface. The effect of weather on the ability to maintain close control cannot be over emphasized!

To maximize the efficiency of any chemical treatment, it should be used continuously and only to the extent necessary. The latest and most efficient method used today is the "continuous treatment" method developed by Tiff Hilton at Leckie Smokeless Coal. The ammonia vapor is injected at the entrance channel to the pond where it is evenly dispersed into the pond. Where flows are constant, such as ponds being fed by water pumped from deep mines, a simple manual system can be installed. The system components are, the storage tank, a 1/2" or 3/4" steel pipe line, a needle valve for control and a check valve to prevent water from coming back into the storage tank. Refer to Drawing 1.



Drawing 1.

When ammonia is used in vapor form, the vaporization of the liquid in the storage tank requires heat. This heat is taken from the ammonia liquid remaining in the tank which is gradually replaced by heat from the surrounding air. In winter weather, little heat is available from the surrounding air and the storage tank will become very cold. Since the vapor pressure of ammonia is dependent on its temperature, the pressure can become very low. When this pressure is being used to motivate a feed system, the variation in pressure causes variation in feed rate and poor control.

Variations in pressure may be eliminated by using a pressure regulator and/or an electrically operated vaporizer. The vaporizer maintains pressure by providing the heat required to vaporize the ammonia. An electrically powered vaporizer will be provided by National Ammonia with a storage tank at no extra charge. Additional information on a vaporizer is available in the pamphlet "Storage & Handling of Anhydrous Ammonia". Note that a pressure regulator will lower the pressure and hold it at a fixed level but it cannot raise the pressure.

The operation of the "continuous treatment" method may be improved by the use of a proportioning valve, a proportioning pH controller and a pH probe. With this system, gradual changes in water flow rate, water pH and ammonia flow rate cause gradual changes in the proportioning valve setting resulting in closer control of feed rate.

As an added "built-in safeguard", where power is available, we recommend a pH probe control instrument connected to a solenoid valve located at the storage tank. If the pH reaches the high set point due to low water flow, a malfunction, tampering etc., the entire system would shut down before an excessive amount of ammonia could be discharged into the receiving stream.

Ammonia buffers itself at approximately 9.2 pH. This is probably the most significant fact which should be fully understood when using ammonia for a specific application. Whether using ammonia, sodium hydroxide or any other chemical, one should treat the water only to the degree necessary to meet the effluent limitations.

In coal mining, there are basically three different limitations on the effluent which must be met. These limitations are on pH, Iron and Manganese. Each of these requires a different level of treatment to meet effluent limitations. It is possible for all three problems to exist with the same water, but generally this is not the case.

Example 1: The water being treated is low in pH and both iron and manganese are absent. Treatment in this case would not need to exceed a 7 pH and legally the pH could be maintained between a 6 and 7 pH.

Example 2: The water being treated has an iron level exceeding the effluent limitations. The pH may or may not be acceptable but this is irrelative if the plan is to precipitate the iron based on pH. There is no manganese in the water. In this case, without using chemicals (such as flocculants or Ultrion, an oxidizer), treatment in this case would probably require that the pH be raised to between an 8 and a 9 pH.

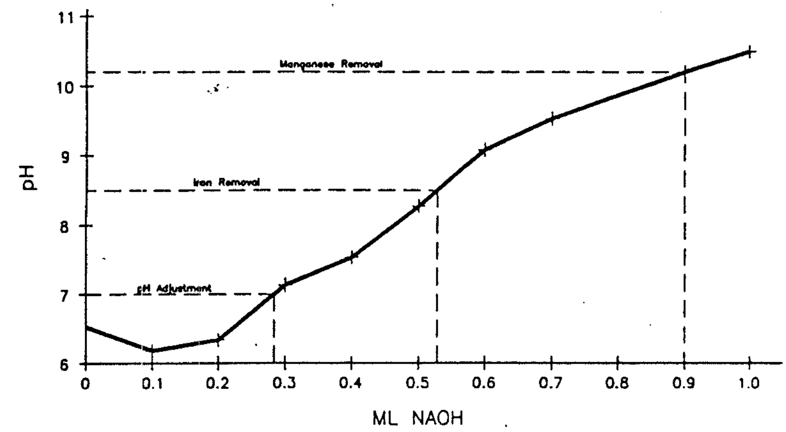
Example 3: This water has a manganese content which exceeds the effluent limitations. Again, the iron content and pH are irrelevant if the intention is to take out manganese by pH alone. In this example, the pH should be raised to a 9.8 if ammonia is used or to 10 or 10.4 pH if sodium hydroxide is used. Because all waters are different, these values may vary .

Following are two examples of actual titration curves. In these examples, sodium hydroxide is being compared to ammonia. In Fig. 2, notice how the ammonia begins to buffer itself around a 9.2 pH.

In this example, Aqua ammonia (29.4 % by weight of ammonia in water) was used instead of 100% anhydrous ammonia. Had anhydrous ammonia been used, the amount required to generate a 9.8 pH would have been 0.9 ml. x .294 or .26 ml. instead of the 1.0 ml. indicated.

The actual cost of the treatment is illustrated in Figure 3. These cost figures are based on 1990 prices for material purchased in bulk. Note that there is a considerable cost differential between ammonia and sodium hydroxide to achieve a specific pH. However, as in the titration curves, the gap begins to close as the pH increases. Even with this closing gap, ammonia is still 50% more cost effective for manganese removal and as much as 85 to 90% more cost effectve for iron removal. Figure 2. also demonstrates how important it is to "fine tune" the feed

NAOH TITRATION TEST

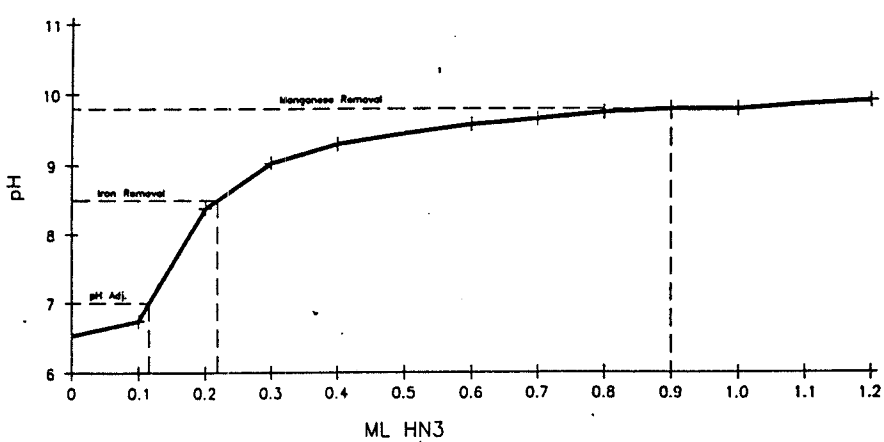


NOTES: .28 ml required to raise the pH from 6.53 to 7.00
0.53 ml required for Iron removal
0.90 ml required for Manganese removal

This graph represents an actual titration of a sample of acid mine drainage. Titration tests of other site specific samples may yield different results.

FIGURE 1

NH3 TITRATION TEST



NOTES: 0.12 ml required to raise the pH from 6.53 to 7.00
0.22 ml required for Iron removal
0.90 ml required for Manganese removal

This graph represents an actual titration of a sample of acid mine drainage. Titration tests of other site specific samples may yield different results.

FIGURE 2

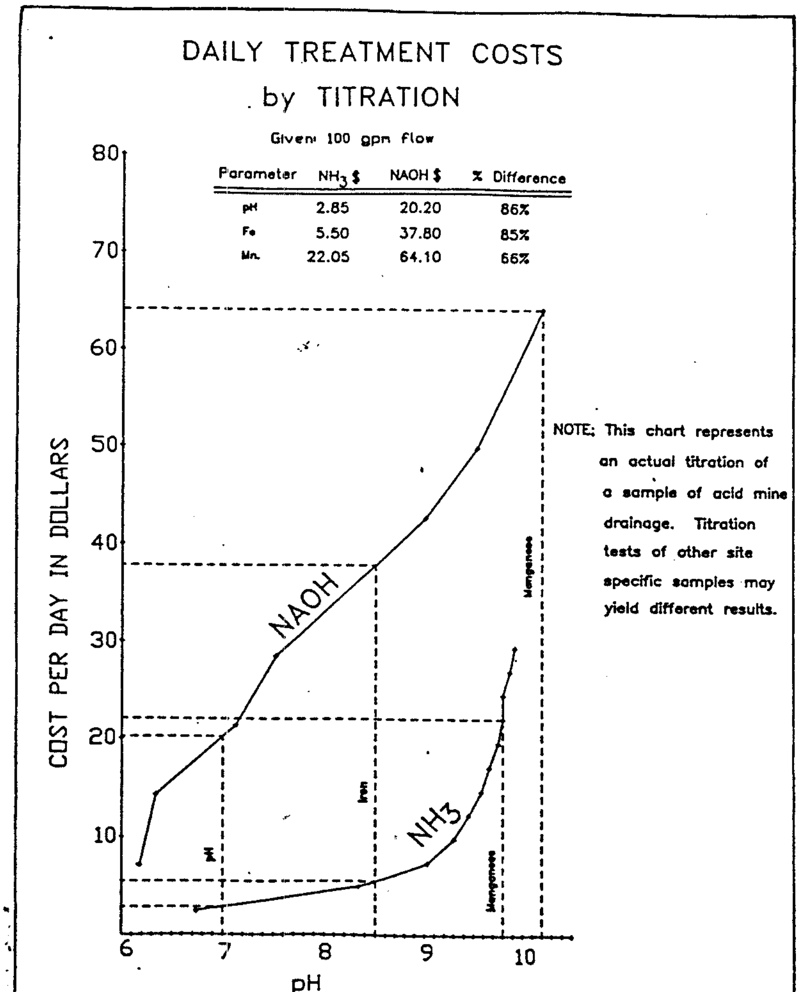


FIGURE 3

system so as not to over treat. Samples should be taken and curves prepared for each planned treatment site.

Ammonia may also be used in coal preparation plants safely and without odor. It will not adversely affect the flocculents used in the plant and the gelatinous precipitate formed will assist in clearing the fines. Ammonia can be added as a vapor when close control is required or as a liquid when rapid neutralization is required. This flexibility is a great advantage for plants that wash several different seams of coal where each has a different effect on pH control. Ammonia has been introduced to the froth cells and to the thickener. This application usually involves a tank, piping, a proportioning valve, a check valve before the thickener, a pH probe in the pipe, a pH controller and a strip chart recorder.

Estimates of the quantity of ammonia which will be required for a given situation may be made by using the "Equivalent Acid Neutralizing Capacity" shown in Table 1. Where no previous experience is available, a sample quantity of water should be taken (5 gallons), the water treated with one of the listed materials until the desired results are obtained and the equivalent amount of ammonia calculated.

Equivalent Neutralizing Capacity to One Pound of Anhydrous Ammonia	
Aqua Ammonia, 26° Bé	3.40 lbs.
Liquid Caustic Soda, 50%	4.76 lbs.
Flake, Bead or Solid Caustic Soda	2.35 lbs.
Soda Ash	3.12 lbs.
Burnt Lime, 95%	1.77 lbs.
Limestone, 90%	3.28 lbs.

Table 1.

Following are some important properties of anhydrous ammonia.

1. Ammonia is lighter than water; water solutions of ammonia are lighter than water.
2. Ammonia boils at -28° F.
3. Ammonia has a molecular weight of 17.032.
4. Ammonia is not compatable with copper, brass, zinc or any alloys of copper. Use only steel or stainless steel hardware.
5. Anhydrous ammonia liquid is colorless.
6. Ammonia reacts with water in two ways:

(a) It directly combines with hydroger ions (acidity) to form NH_4.

(b) It combines with water to form $NH_4 + OH$, leaving the hydroxyl ion formed to combine either with the metals or with hydrogen ions.

7. Inventories and releasés of anhydrous ammonia are reportable under the S.A.R.A. Title III Regulations (Community Right-To-Know Act).
8. Ammonia does not accumulate in the body, but is processed and discharged daily as a normal body function
9. The use of ammonia requires modification of your N.P.D.E.S. permit.
10. Ammonia buffers itself at approximately 9.2 pH.
11. Aqua solutions of ammonia act as solvents rather than precipitators which can result in over treatment unless close control is exercised.
12. Exposure limits for ammonia established by OSHA are 35 ppm short term exposure (STEL) and 25 ppm time weighted average (TWA).

<u>Sources for System Hardware</u>:

Valves, Solenoid Valves, Pressure Regulators, Pressure Gauges:

National Ammonia Co..................800-643-6226

(in Pennsylvania)...800-643-2626

pH Instrument:

Data Aquisition System...............412-327-8979

Great Lakes Instruments Inc..........414-355-3601

Back Check Valves:

Analabs..............................304-255-4821

Continental NH3 Products.............800-537-5642

Hansen Technologies Corp.............800-426-7368

Ammonia Hose:

Goodall Rubber Co....................609-587-4000

Dayco Corp...........................513-226-5923

If you are considering the use of anhydrous ammonia at your site for water treatment, the following steps are suggested:

1. Analyze your receiving streams for existing total nitrogen, ammonia, nitrites, nitrates, pH and sulfates. You may be located in an area where the existing ammonia level is too high already and the addition of more ammonia could damage the stream environment. This happens in areas located near farm drainage, raw sewage sources, hatchery effluent etc.
2. If you find the stream quality low or absent of ammonia, proceed by performing a Benthic study of your receiving stream. Study above and below the confluence of the discharge and the stream. Contention is that ammonia treatment can cause problems associated with the micro- and macro-communities so it is wise to document your pre-ammonia water quality. Also, there exists a fear that acidity will be created downstream as ammonia is nitrified. So far, this has only been demonstrated in the laboratory and not in the field.
3. Request in writing, to the State, to modify your NPDES permit to include ammonia as a chemical to treat water at your site. Be sure to include your background data to justify your request. If approved, you will be sent DMMR's which require that you sample the stream for total ammonia converted to un-ionized ammonia, nitrites, nitrates and pH. Un-ionized ammonia has proven to be harmful to aquatic life and, based on limits established by the Water Resources

Board, must be kept less than .02 PPM in trout streams and less than .05 PPM in all other streams. Un-ionized ammonia is calculated, using total ammonia, temperature and pH by use of the following formula.

$$\text{Un-ionized Ammonia} = 1.2 - \frac{\text{Total Ammonia} - N}{1 + 10^{(pKa - pH)}}$$

$$\text{Where} \quad pKa = 0.0902 + \left[\frac{2730}{273.2 + T\,°C} \right]$$

4. With your NPDES permit approved, determine the quantity of ammonia you will require and the storage capacity you will need. The quantity of ammonia you will use can be determined by calculating the ammonia equivalent to other chemicals you may have used in the past or by treating a sample quantity of water to obtain the required results and multiplying this amount by the total quantity of water to be treated. If your lab is not capable of performing a titration test, contact National Ammonia Company and we will arrange to have a raw water sample taken and a titration performed for you.
   Assuming a minimum two week delivery cycle and a 70% useable tank capacity, your storage requirements can be estimated. Tank sizes commonly available are 1000, 10,000, 12,000, 15,000, 18,000, 25,000 and 30,000 gallons. Contact your National Ammonia Company Sales Representative for information on the tanks and other hardware you may require.
5. Once you know tank sizes and locations, you must comply with SARA

Title III and Community Right-to-Know laws by notifying your local fire department, your Local Emergency Planning Commission (LEPC) and your State Emergency Planning Commission.

6. Establish your monitoring parameters. I would advise several downstream sampling points in addition to that required by your permit and monitor for pH, Total Ammonia, Nitrates, Nitrites and Dissolved Oxygen. Downstream results should be constantly compared with upstream samples.

7. Finally, the use of ammonia is not for everyone. It should be used only by responsible persons who will use it safely and constantly monitor the results of its use and its effect on the environment.

Acknowledgements:

John Adair, National Ammonia Company

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Ron Lilly, Analabs, Incorporated