



# Ammonia

Improved equipment and techniques put all-ammonia pipeline into service from Texas and Louisiana to Midwest consumption areas. New doors for similar transportation of other fertilizer products may soon be opened.

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MODERN ALL-WELDED PIPELINES built over the past 15 years have achieved an outstanding record for safe and dependable operation. Particularly, in the period since World War II, technological advances have occurred rapidly in all phases of pipeline work. With better steel pipe now available, better welding and inspection techniques and utilizing the most advanced design and safety features, it is apparent that a completely new pipeline system can be built for mass transportation of anhydrous ammonia. The system will be a distinct improvement over present transportation methods, both from the standpoint of economics and public safety.

On this basis, Gulf Central Pipeline Co. was organized to build and operate a pipeline to transport anhydrous ammonia from the major producing regions along the Texas and Louisiana Gulf Coast for distribution to the major corn belt consuming areas in Iowa, Illinois, Nebraska, Indiana and Missouri. The company,

◀ Figure 1. Gulf Central Pipeline system.

Pipeline construction specifications call for 36 in. of cover, but allow for 48 in. where deep plowing methods are used.



# Transport via Pipeline

an independently owned and operated common carrier pipeline, will be subject to regulation by the Interstate Commerce Commission. The pipeline is extended to serve all producers and marketers desiring to ship anhydrous ammonia. The Gulf Pipeline is expected to provide both economy and safety for the domestic fertilizer industry in its problems of transportation, distribution and delivery of anhydrous ammonia to meet seasonal demands.

## The pipeline system

The Gulf Central Pipeline system, illustrated in Figure 1, may be functionally divided into three general sections: gathering, trunkline and distribution. The gathering sections will service the major ammonia producing centers in the Texas and Louisiana Gulf Coast. One leg of this section will service plants along the lower Mississippi River generally between New Orleans and Baton Rouge. This leg, an 8 in. line approximately 112 mi. long, will intersect the main trunkline near Alexandria, La. A second leg will service plants in Western Louisiana and Texas and will be constructed as requirements dictate. The 10 in. trunkline section will extend from Central Louisiana near Alexandria and run a distance of approximately 548 mi. North through the center of Arkansas and Missouri to Hermann, Mo. The line will generally run parallel to, and about 50-100 mi. West of the Mississippi River.

Additional gathering and distribution lines will tie into this main trunkline system as requirements dictate. The distribution section will originate at Hermann, Mo., the northern end of the trunkline, and

will initially consist of two laterals, each a combination of 8 in. and 6 in. lines. One lateral, running East into Illinois and Indiana, will consist of approximately 234 mi. of 8 in. line which will reduce to 6 in. near Terre Haute, Ind. for an additional 153 mi. to Columbia City, Ind. The 8 in. West lateral will run northwest into Iowa for approximately 417 mi. and will reduce down to a 6 in. line at Spencer, Iowa. The 6 in. line will continue for 234 mi. southwest from Spencer, cross the Missouri River into eastern Nebraska and terminate at Aurora, Neb.

## Proposed operation

Agricultural or commercial grade anhydrous ammonia shipped via the Gulf Central Pipeline will be flowing as a liquid between 35°F and 75°F, the temperature being a function of the ground temperature conditions. The ammonia will be tendered on an average daily rate to the pipeline and will be interchangeable. Thus, a minimum product specification must be met, as shown in Table 1. The pipeline fill will be owned by Gulf Central and any losses will be absorbed by the Pipeline Co. through purchase of additional line fill. Since liquid ammonia is essentially incompressible, a tender to the system will be offset by virtually an immediate displacement delivery of equal quantity to the shipper at designated delivery point(s). Surplus capacity, if available, will be offered on a short term basis for spot or batch tenders.

At atmospheric pressure and temperatures above -28°F, anhydrous ammonia is a gas lighter than air. Thus, upon release in open areas, the ammonia gas rises to higher altitudes and has no tendency to settle

near the ground in such places as river bottoms, valleys and other topographical depressions.

The flammable limits at atmospheric pressure are 16-25% by volume of ammonia in air. Experiments conducted by a nationally recognized laboratory indicated that an ammonia-air mixture in a standard quartz bomb does not ignite at temperatures below 1562°F (1).

Experience has shown that ammonia gas and air mixtures, even when occurring within the narrow range of susceptible proportions, are extremely hard to ignite and burn with little vigor. Anhydrous ammonia in both the liquid and gaseous states is extremely soluble in water. Gaseous ammonia will irritate the skin and mucous membranes. At 55 ppm its odor is detectable by most people and at concentrations of 5000 ppm or greater it can be fatal. Because it serves as its own warning agent, no person will voluntarily remain in concentrations which are hazardous.

While anhydrous ammonia does not attack steel, it has been determined that contaminants in ammo-

**Table 1. Anhydrous ammonia specifications.**

Ammonia	99.5% minimum by weight
Water	0.2% minimum by weight
Oil	4 parts/million maximum
Inerts	0.5 cc/gram maximum
Temperature	35°F minimum— 85°F maximum
Pressure	300 PSIG minimum— 1450 PSIG maximum

nia such as carbon dioxide and air can cause stress corrosion cracking. Normal operating conditions of the pipeline will exclude the presence of carbon dioxide and air. In addition, ammonia transported via Gulf Central Pipeline will contain at least 0.2% water (2000 ppm).

The pipeline transportation of liquid anhydrous ammonia involves no unusual difficulties or problems not normally encountered in similar transportation of liquified petroleum gases. If anything, it is less hazardous due to its limited flammable nature, high specific heat and heat of vaporization, and relative vapor lightness.

Although the presence of 0.2% water in anhydrous ammonia effectively inhibits stress corrosion in steel (2), the pipe specifications for the Gulf Central Pipeline project specify a steel material that would further avoid the possibility of stress corrosion and prevent the occurrence of pipeline ruptures. A study was made to consider the metallurgy required for transporting the gas by pipeline in 6, 8 and 10 in. size at a maximum pressure of 1440 psig and a temperature range of +35-+75°F.

### Pipe grade chosen

Based upon this study, Grade X42 pipe (having minimum yield strength of 42,000 psi) was chosen instead of a higher strength grade such as X46 or X52 pipe normally used on LPG pipelines. Prevention of residual pipe stresses can be accomplished in part by grade selection. The grade with the lowest strength probably would have the lowest internal residual stress and therefore should be the best choice. Grade B pipe, having a lower strength than Grade X42 was considered. As a practical matter, most steel companies furnish X42 for Grade B as an economy in pipe manufacture. According to code stipulations, the pipe wall thickness required for a given operating pressure varies inversely as the pipe grade specified. For example, at the same design operating pressure, a pipeline constructed with Grade X42 pipe would require a wall thickness 23.8% greater than with Grade X52 and 9.5% greater than with Grade X46.

Anhydrous ammonia will rapidly corrode zinc, tin, copper and copper base alloys such as brass. The copper content in the pipe has been limited to a maximum of 0.15%. This residual copper is in solution in the steel

and is not attacked by ammonia.

The maximum pipe transition temperature has been set at 0°F which is substantially below the 35-75°F normal operating temperature range of the system. At operating temperatures above the transition temperature, pipe failures are largely ductile shear failures, while at temperatures below the transition temperature, failures are predominantly brittle fractures. Ductile shear failures are localized in nature whereas brittle fractures have been known to propagate along the pipeline at a velocity approaching the speed of sound. The length of a pipeline affected by a possible rupture could be quite large if a brittle fracture occurred whereas a ductile shear fracture, would be completely localized.

The pipe manufacturing process is specified as the electric resistance welding process and the pipe is furnished in the nonexpanded condition with no cold expanding after forming and welding. The API Standard 5LX latest revision was used for reference specification. Testing of the steel for the pipe includes ladle analysis, transverse tensile properties, weld tensile and flattening tests. In performing the weld tensile test, Charpy V-notch impact tests are performed on the plate, center of the weld and heat affected zones. The testing is performed in accordance with ASTM A-333 except the V-notch is used. Each pipe section is heat treated and hydrostatically tested at 1760 psig. The non-destructive testing includes testing of all welded seams by radiological, ultrasonic or electromagnetic methods after heat treating and hydrostatic testing are performed. All pipe will be inspected by a representative of Gulf Central Pipeline.

### Special efforts

In addition to the safety considerations given to the metallurgical specifications of the pipe, further special efforts have been made in design and planning the pipeline system to conform to all local, state, Federal and engineering code requirements. These requirements are exceeded in many design phases. Gulf Central requires that all reasonable efforts be taken to insure a sound and safe design and operation of the pipeline system.

The pipeline system is being designed to conform to the ASA B 31.4 -Liquid Petroleum Transportation Code and the ASA B-31.8 Gas

Transmission Code, where the latter is more stringent than the B-31.4 code. This design criteria has resulted in using heavier walled pipe where the population density index dictates. The population index criteria is not generally used in the design of comparable LPG pipeline systems.

The pipeline routing has been selected across open agricultural and barren lands wherever practical, thereby avoiding densely populated areas. Pump station and terminal sites are similarly located in low habitation areas.

At major river and water crossings, Grade B seamless pipe of ½ in. wall thickness will be installed. This is considerably heavier construction than normally required.

Main line shut off valves are normally installed in open areas at intervals not to exceed 20 mi. As an added precaution on the Gulf Central Pipeline project, these valves will be installed at approximately 10 mi. intervals. On the 8 in. gathering lines and 10 in. main trunkline, check valves will be installed adjacent to each main line valve. The valves will offer an additional safeguard in event of a line break in that all pipeline contents ahead of the rupture site would be prevented from back flowing to the rupture point.

At pump station locations and major river crossings, sensing equipment will be installed which can detect line breaks or ruptures by the resultant sudden changes in pressure. This equipment will activate automatic shut off valves which will isolate the rupture in a pipeline section.

Construction specifications call for the pipeline to be installed with a minimum of 36 in. cover. When the pipeline crosses areas where deep plowing methods are used, 48 in. cover will be provided.

It is planned to install a greater number of more conspicuous signs and markers than normal along the pipeline route.

After the pipeline is constructed and tested, it will be purged and filled at all times with ammonia so that no air, oxygen or carbon dioxide can be admitted.

### Pipeline rupture

A pipeline break or leak on a well constructed and operated pipeline is relatively rare. However, if it does occur, it is essential that the behavior of ammonia under such circumstances be understood and proper

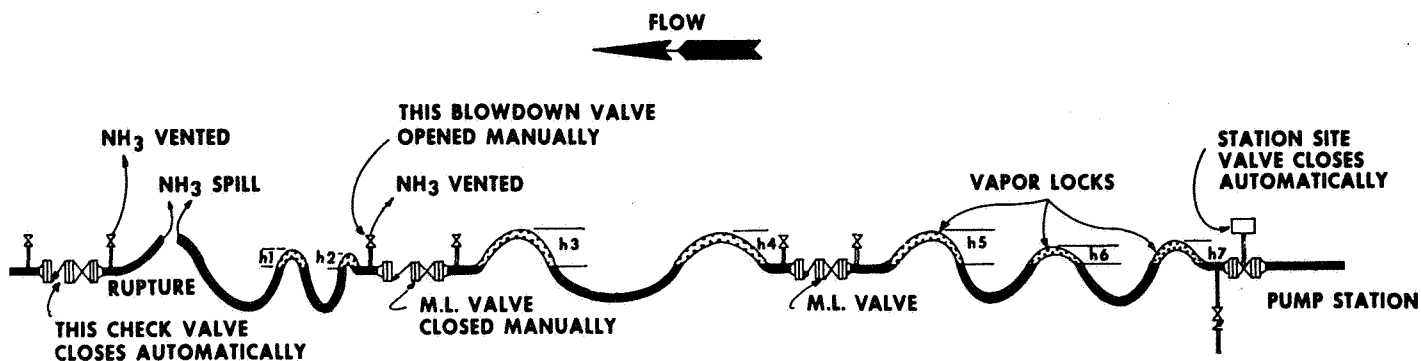


Figure 2. Conditions existing after a pipeline rupture.

action be immediately taken to minimize any dangers.

An engineering evaluation of such situations occurring on the Gulf Central Pipeline system follows:

### I. Large Pipeline Rupture

#### A. Estimate of Conditions Occurring in Pipeline:

In the event of a major line rupture, the downstream check valves would close, as seen in Figure 2, the upstream line break detector would close a main line shutdown valve at the upstream station site. Pumps at the upstream pump station would automatically shutdown. The low pump suction shutdown controls at all of the downstream pump stations would shut in these stations. Upstream stations would automatically shutdown because of rapid pressure decline. The pipeline break would be isolated to that section lying between two pump stations. An initial high pressure spurt of ammonia would quickly subside as pipeline pressure is vented. Liquid ammonia is relatively incompressible and the driving force for ammonia exiting through the rupture would be the vapor pressure of ammonia at line flowing temperatures, i.e., 107 psia @ 60°F.

As liquid flows out of the rupture, a volume of liquid is vaporized within the pipeline to form gas pockets which seek the high spots along the pipeline route. These pockets in effect, form a series of "vapor locks" at every hump along the pipeline. These locks greatly

reduce the flow out of the rupture as they cause a back pressure to flow due to the accumulated heads created by each rise in the pipeline which is capped with a gas pocket.

It is thought that the discharge of ammonia at the rupture will quickly become a lengthy, spasmodic ejection of liquid and vapor combination.

The flashing of liquid within the pipeline will also produce a cooling effect on the remaining liquid. The cooler remaining liquid will consequently have a lower vapor pressure which reduces the driving force to flow.

To summarize after a pipeline rupture, there will be a momentary surge of flow followed by a rapidly decreasing rate of discharge leveling off to a prolonged period of spasmodic, combination liquid-gas discharges common to two phase flow pipelines.

Three main factors which tend to quickly reduce flow are:

1. Immediate shutdown of pumps and line pressure release.

2. The vapor locks in each pipeline hump created by liquid flashing to vapor to fill displaced volumes.

3. The reduction in the vapor pressure of the liquid ammonia in the pipeline due to the flashing of liquid to vapor. As liquid flashes to vapor, the necessary heat of vaporization is withdrawn from the liquid thereby causing the remaining liquid to cool. The vapor pressure of the liquid will decrease

with the lowering of temperature.

#### B. Estimate of Conditions Existing Outside Pipeline:

Immediately following a pipeline rupture, a momentary discharge of high pressure ammonia liquid occurs which will flash to gas. This will be followed primarily by a liquid ammonia stream collected in pools in low spots. As the liquid evaporates, it will cool instantly and reach -28°F. The evaporation rate is fairly slow (1 to 7 lbs./hr./sq. ft. of surface area.) (3).

The evaporated ammonia gas will rise rapidly since it has approximately the same weight as pipeline natural gas and is lighter than air.

A relatively small area will contain a large volume of liquid ammonia. For example, a 10 mil. section of the 10 in. main pipeline (maximum section in Gulf Central's pipeline) contains 591 tons of ammonia at 60°F. Assuming that 90% by weight will remain as a liquid at -28°F during a line break, this weight of ammonia or 24,990 cu. ft. volume wise could be entrapped in the following areas:

Depth In.	Sq. Ft.	Side of Sq. Ft.	Acres
24	12,495	112	0.29
12	24,990	158	0.57
6	49,980	224	1.15
4	74,970	274	1.72
2	149,940	387	3.44

In the worst case, the spill is confined to a relatively small area.

#### C. Repair Procedures—Large Rupture:

Any major pipeline break will be detected immediately by the pipeline dispatcher. He will know that the location lies between two specific pump stations. Men will be dispatched to close all main line pipeline valves between these stations and locate the break. The blow-down valves located between the main line valves shutting off the ruptured pipeline section will be opened and ammonia vented. This action will accelerate the formation of "vapor locks" and reduce the ammonia spill volume at the rupture site.

The initial goal will be to contain the ammonia spill in a compact area by diking around the spill and evacuating people and animals directly adjacent and downwind of the rupture. Depending on the site and wind conditions, excavating equipment may be used to uncover the ruptured area. After the liquid pool subsides, the ruptured section can be cut out and a new piece inserted.

If working conditions at the rupture site prevent this action, stopple plugs can be inserted a short distance on each side of the rupture, the flow stopped, and the repairs effected. Stopples are expansible devices which can be inserted into an operating pipeline under pressure to effectively shut off the flow. They can also be removed without affecting pipeline service.

## II. Small Pipeline Leaks

A small leak will generally freeze the ground around the pipe and tend to contain itself. The leaking ammonia would be expected to be mainly in the gaseous state and liquid spills would not be anticipated. Repairs can be made by uncovering the pipeline and installing a permanent or temporary patch. If the frozen earth prevents excavation, stopple plugs can be inserted on both sides of the leak, a temporary bypass line installed, and repairs on the leak effected after the ground has thawed.

## III. Comparison of the Characteristics of Anhydrous Ammonia with those of Propane

The large amount of experience with pipelining propane forms a

definitive background against which ammonia pipeline break and line leak problems can be evaluated.

Both these products have similar vapor pressures at the same temperature and both are good refrigerants when liquid is flashed to gas. Ammonia has a greater toxicity but is relatively non-flammable whereas propane is highly flammable.

Propane liquid is much more easily vaporized than ammonia. In fact, ammonia requires over three times more heat to vaporize a pound of liquid than propane. This would mean that ammonia is much more liable to remain in liquid spills than propane. Propane vapors, being much heavier than air, tend to spread out along the ground whereas ammonia vapors dissipate rapidly and rise quickly.

A small pipeline leak in ammonia service would be quite similar to a propane line leak. The ammonia leak could probably be located easier because of the odor.

A large rupture in an ammonia line would be expected to produce more of a liquid spill than a propane line break. Because propane liquid is much more compressible than liquid ammonia, a greater volume of propane would be initially lost and the initial high rate of discharge would last longer than an ammonia line break.

A comparison of the vapor and cold liquid quantities formed when propane or ammonia liquid are suddenly released to atmosphere is of interest. For each pound of ammonia liquid at 60°F (107 psia) suddenly released to atmospheric pressure, approximately 10% will immediately flash to vapor with the remaining 90% as -28°F liquid (4). Similarly, for a pound of propane liquid at 60°F flashed at atmospheric pressure, 33% will go to vapor with 67% remaining as -44°F liquid. Summarizing, pound for pound, a propane pipeline rupture will immediately produce over three times the amount by weight of vapor that an ammonia line break would produce.

Because propane liquid is more readily vaporized, most of the propane problems will lie in the spread of ground hugging vapors. It would appear that the hazardous area occasioned by a propane pipeline break would be much larger than a similar ammonia line rupture, with more of the dis-

charged ammonia being in liquid form and the vapors formed being dissipated rapidly.

Finally, by nature of their different markets, the chances of an ammonia line rupture occurring in a populated area is substantially less than for a propane line. The line routing of the Gulf Central system will be predominantly through rural areas while propane pipelines frequently service terminals in urban centers.

## In summation

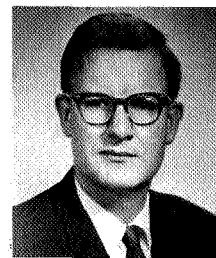
The Gulf Central Pipeline is unique from an engineering standpoint only in that it is designated for safe long distance transport of a new product—anhydrous ammonia. Pipeline transportation which has served the gas and petroleum industries well for so long, will now begin to provide service to the fertilizer industry on a major scale. Safety in handling, distribution and transportation of any product has been the prime concern of the pipeline industry.

Gulf Central Pipeline Co. is committed to realizing this goal of safe transportation through carefully considering the design of an ammonia pipeline system. It is hoped that the impact made by Gulf Central Pipeline will open new doors for pipeline transportation of other fertilizer products. #

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## Discussion

**J. D. REED**, ICE, Ltd., Billingham, England: You said that when ammonia is spilled, as it cools down the ground will freeze. This is not borne out by our own observations and we believe that ammonia penetrates the soil, and any water present goes into solution which generates heat and causes more evaporation.

The other point made was that the ammonia cloud which forms, being lighter than air, will rise. This is only partly true in our view because the ammonia will not remain at  $-28^{\circ}\text{F}$ , but it will cool down to a much lower figure than this. In fact, it will reach a point where mixtures are formed which are as dense or denser than air and these will drift close to the ground.

As part of the normal process operations can the isolation valves be closed, and, if so, what precautions are taken to avoid the locked in volumes expanding and causing a rupture?

**INFOKER**: What I stated in the paper was theory based on as much background information as was available. We will be conducting some tests with pinhole and larger leaks on 6,000 ft. of six in. line and these tests will hopefully provide useful data.

Where a blocked section has a rupture, all of the contents will tend to flow toward the rupture. On the gathering and main line, we have check valves so that if the pressure builds up it will force the liquid to flow in the direction intended. In turn, we have a pressure storage system located at the junction of the main line and the two lateral lines, at which point the ammonia from each of the two eight-inch lateral lines, as well as the main line, can seek storage. We don't have check valves in the eight-inch distribution line because we'll have bi-directional flow during the peak system.

**REED**: One more observation: I gathered from the presentation that if you did get a spill from this pipeline the effects would be very local. A few years ago we had a spill from a pressure source of less than five tons. A wide area up to 200-300 yards downwind and 50 yards upwind became untenable. It was possible to detect ammonia about two miles downwind from the spill.

**ANON**: We spilled between 10-15 tons of ammonia and the cloud kept going along the ground and killed about three cows two miles from the plant. We inconvenienced a small town about six miles from the plant with people having to rush to their outlying homes because the ammonia was unbearable in the shopping district. There may be some atmospheric condition of temperature and pressure where the ammonia cloud will stay on the ground and propagate very slowly toward habitations.

**ANON**: No comment has been made about the effect of water. Water in the atmosphere and water in a water course

or in a drain in the spill can cause problems. On an occasion where about 10 tons were spilled in a period of 20 minutes, the cloud not only hugged the ground, but it was also an impenetrable fog as far as visibility was concerned. The people involved in rescue operations had to feel their way through the cloud.

**WALT HOWARD**, Monsanto Co.: I'd like to make a further comment about the distance that ammonia might travel. True, ammonia is lighter than air, but ammonia can travel a very great distance at ground level, even without requiring the presence of water vapor. When any gas is mixed with air, down to a low concentration of that gas in air, the total gas mixture of air with the other gas then has a density, or if you please a molecular weight, almost the same as that of air. For example, a one per cent ammonia, 99 per cent of air mixture is going to have a density so close to that of air that it will behave essentially like air. The fact that ammonia by itself is lighter than air does not mean—definitely does not mean—that the molecules of ammonia are going to rise through the molecules of air. Once they're mixed, the gas mixture is a homogeneous mixture and stays mixed.

Therefore, the low concentration ammonia-air mixture, without requiring any water vapor, without requiring any special atmospheric conditions, can travel for great distances. The only thing which really limits in this case is the further mixing of the ammonia in the air by natural mixing processes such as turbulence creation or diffusion itself, which latter of course would be very slow, to get the ammonia down to still lower concentrations.

Now I think you recognize that toxic concentrations of ammonia begin at very low ammonia concentrations. This therefore means that you can in fact have very dilute yet highly toxic ammonia-air mixtures at considerable distances. So don't count on ammonia being light and rising as a cloud. I think a very classic example that shows this very well is a particular methane spill that some of you may know about, and this was methane which spilled at ground level, then went about 500 feet at ground level and there found an ignition source, an open-fired heater. The methane-air mixture was still in a flammable range. The flame flashed back from this ignition source to the source of the methane spill. On the way back it blew up a building. This, in turn, caused a very large loss in this plant.

Now methane has about the same molecular weight as ammonia, but with even a five per cent concentration with air, which is about the lower flammability limit, has a density about the same as air. It's going to behave about like air and will have little tendency to rise in air. This is a misconception that appears to be often held.